

BIBLIOGRAPHY ON EXTRACTIVE METALLURGY OF NICKEL AND COBALT, JANUARY 1929—JULY 1955

BY R. B. BAUDER

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PREFACE

This bibliography and abstracts of the literature on nickel and cobalt covering the period January 1929–July 1955, which was prepared as part of the Bureau of Mines research program on Cuban laterites and serpentines, is being published as a convenient reference and aid in the research on and investigation of the ores and products containing these metals.

A similar bibliography is being prepared for the literature covering 1900–29, during which some outstanding work was performed on extractive metallurgy of nickel and cobalt. The Bureau proposes to publish this material in a companion circular at an early date.

BIBLIOGRAPHY ON EXTRACTIVE METALLURGY OF NICKEL AND COBALT, JANUARY 1929–JULY 1955¹

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R. B. BAUDER²

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¹ Titles enclosed in brackets are translations from the language in which the item was published.

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³ For mechanical treatment, see Ore Dressing; Metallurgical Products (p. 29); for hydro treatments, see Hydro Treatments of Matte and Speiss (p. 83); for electro treatment, see Electrometallurgy (p. 109).

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INTRODUCTION AND SUMMARY

In connection with a Bureau of Mines research program on utilization of Cuban lateritic ores, a comprehensive review was made of the chemical literature on nickel and cobalt. Initially, the review had as its objective the selection, from the voluminous literature dealing with the chemistry of these two metals, of only those references to reactions that were especially pertinent, or at least closely related, to the field of extractive metallurgy. Later, the coverage was extended to include references to the techniques and plant applications of extractive metallurgical procedures for the recovery of nickel and cobalt.

In this report, the period from January 1929 to July 1955 has been covered, as it seemed logical that recent literature should be of greatest value. This cutoff date was established in order that the bibliography could be issued at an early date, inasmuch as currently much work is in progress on the lateritic ores. Later, a supplement will be prepared extending the coverage to about 1900.

The indexing and abstracting services consulted were *Chemical Abstracts*, 1929-55, under all headings starting with "nickel" and "cobalt"; *Engineering Index*, 1935-54, under the headings "nickel metallurgy" and "cobalt metallurgy" and citations crossindexed under them; *British Abstracts*, volumes B-1 and A-1, 1935-53, under subjects starting with "nickel" and "cobalt" (unfortunately, fully half of these volumes were missing from local files); *Metals Review*, 1950-53; United States Government Publications Monthly Catalog, issued by the Superintendent of Documents, United States Government Printing Office, 1941-54; Bureau of Mines publications, 1910-July 1955.

The author wishes to gratefully acknowledge free use of *Chemical Abstracts*. Many abstracts have been copied verbatim; some have been shortened or otherwise altered; others have been merged with citations from another literature index referring to the same original. Although *Chemical Abstracts* has been the major source of information, *British Abstracts*, *Engineering Index*, and *Metals Review* have also contributed materially.

Several possible arrangements of references were considered. That chosen as most practicable comprises five main parts: (I) General Metallurgy, (II) Pyrometallurgical, (III) Hydrometallurgical, (IV) Electrometallurgical, and (V) Miscellaneous; each part was subdivided into main headings, which are further subdivided. "Nonspecified Ores" includes citations applicable to both oxidized and nonoxidized ores, as well as reports that do not indicate the type of ore treated. Under "Oxidized Ores" will be found oxidized ores, silicate oxide ores, and oxides. The subdivision "Nonoxidized Ores" includes all ores not covered by the first two subheadings, such as sulfides and arsenides. A grouping entitled "Studies," under parts II, III, and IV lists theoretical discussions on such subjects as thermodynamic equilibria, crystal structure, and electrical passivity in electrowinning a metal. Most of this group of references include no annotations. Under part V, two primary headings, "Recovery as a Byproduct" and "Recovery From Scrap Sources," seemed necessary to cover some of the material. The primary groupings "Refining of Metal; Pyrometallurgical," and "Refining of Metal; Electrometallurgical," terminate the bibliography.

Omitted for the sake of brevity are all references to mining, mineralogy, or geology alone and statements of production, reserves, etc. A very few references have been omitted for security reasons. A number of references have been deleted because their meaning was obscure, because the metallurgical

operations were questionable, or because of the opinion that their inclusion would add nothing to the cumulative metallurgical knowledge expressed in the other references.

ACKNOWLEDGMENTS

The Bureau greatly appreciates the interest shown by the General Services Administration in the recovery of critical materials. The cost of preparing this comprehensive bibliography was partly defrayed by that agency under Contract GS-00-B (D)-1521.

SELECTED LITERATURE-ABSTRACTING SERVICES

1. AMERICAN CHEMICAL SOCIETY. Literature Resources for Chemical Process Industries. *Advances in Chem. Ser.*, vol. 10, 1954, pp. 438-551; *Chem. Abs.*, vol. 49, 1955, p. 2641g.

In the general section, indicative chapter headings include: Basic Principles of Literature Searching, by Julian F. Smith and Charlotte M. Schaler, pp. 438-440. Sound and Unsound Short Cuts in Searching the Literature, by Charlotte M. Schaler and Julian F. Smith, pp. 441-448. The French Chemical Literature and Its Use, by Ernest F. Spitzer (Chas. Pfizer & Co., Inc., Brooklyn, N. Y.), pp. 487-493. The Japanese Chemical Literature, by L. J. Stevens (Smith, Kline & French Laboratories, Philadelphia, Pa.) and Shinichiro Fujise, Tohoku University, Sendai, Japan, pp. 494-499. The Italian Chemical Literature, by Leo J. Stevens, pp. 500-504. Foreign Alphabetization Practices, by Ernst Van Haagen, 126 E. 31st Street, New York, N. Y., pp. 510-519. Abbreviations in the German, French, and Italian Literature, by Henry Fischbach (Language Service, New York, N. Y.), pp. 510-519. Translating German, French, and Italian Chemical Literature, by Henry Fischbach, pp. 520-528. Transfer of Language Training From German (and English) to Swedish, by Ernst Van Haagen, pp. 529-540. Pitfalls of Transliteration in Indexing and Searching, by M. Hoseh (United States Library of Congress, Washington, D. C.), pp. 541-547. Reviews with many references.

2. BATTELLE MEMORIAL INSTITUTE, Columbus, Ohio. *Review of Literature*, vol. 3, 1946, prepared for members of American Society for Metals. *Am. Soc. Metals*, Cleveland, Ohio, 1947, 811 pp.; *Eng. Index*, 1948, p. 757.

An annotated survey of articles and technical papers in American and foreign engineering, scientific, and industrial journals and books is presented. Subjects ranging from ores and raw materials through industrial uses and applications of the finished product are covered. The addresses of 300 publications covered are given. Author and subject indexes are provided.

3. HISLOP, M. R. Extracts From "The Technical Society as a Library Resource." *Trans.* 41st Ann.

Convention, Special Libraries Association, 1951, pp. 106-119. Abstracting Journals, a Comparative Survey. *Metals Rev.*, vol. 25, No. 6, item 218-A, June 1952, p. 24.

Four metallurgical abstract services were analyzed on the basis of five aspects: Kind of abstract, whether informative or indicative; timeliness; selectivity source material; and subject matter. The services analyzed are ASM Review of Metal Literature; Metallurgical Abstracts (Institute of Metals); Abstracts of Current Literature (Iron and Steel Institute); and Chemical Abstracts (A10).

4. MILEK, J. T. (Richard Rimback Associates, 921 Ridge Ave., Pittsburgh 12, Pa.) Guide to Foreign Sources of Metallurgical Literature. *Metals Rev.*, vol. 24, No. 11, item 267-A, November 1951, p. 24.

Nine sections give lists of foreign metallurgical associations, societies, institutions; periodicals, transactions, proceedings; metallurgical abstract services; foreign standardizing organizations; statistical sources, directories of metallurgical industries; metallurgical books, bibliographies, technical and special reports; and metallurgical abbreviations.

5. MOND NICKEL CO., LTD. (Sunderland House, Curzon Street, London, W. 1, England.) Nickel Bulletin. Abstracting and Indexing Sources for Literature on Metals and Metal Fabrication, by Ellis Mount, 1953, p. 11, John Crerar Library, Chicago, Ill.

A limited number of abstracts on extractive metallurgy are given. *General Description.* Material is restricted to Ni and its alloys; it includes chemistry, metallurgy, properties, plating, corrosion resistance, etc. Abstracts are informative. Journals and patents are covered. *History and Availability.* It was begun in 1928. 1953 is vol. 26. It is published monthly by the Mond Nickel Co., Ltd., at above address. It is not for sale; information regarding gratis subscriptions is available from the publishers. See Union List of Serials for availability in the United States. *Size.* Approximately 500 abstracts are made per year. No figures are available for journal coverage. *Indexes.* Annual author and subject indexes are given and a decennial index, volumes 1-10.

PART 1. GENERAL METALLURGY

GENERAL NONSPECIFIED ORES

LOCAL METAL ENTERPRISES AND PRODUCING AREAS

6. BALLAY, MARCEL. [Metallurgy of Nickel.] Bull. assoc. tech. fonderie, vol. 9, 1935, pp. 113-121; Chem. Abs., vol. 29, 1935, p. 6186².

Describes Ni ores found in New Caledonia and in Canada and the processes of extracting the Ni.

7. BERTHELOT, C. [Nickel and Chromium in the French Colonies.] Chim. et ind., vol. 29, 1933, pp. 718-723; Chem. Abs., vol. 27, 1933, p. 3176.

Brief description of the Ni and Cr resources of the French colonies (New Caledonia) and of their extraction.

8. BOGITCH, B. [Nickel Industry in the Urals.] Rev. mét., vol. 36, 1939, pp. 421-428; (see Chem. Abs., vol. 34, 1940, p. 349¹); Chem. Abs., vol. 34, 1940, p. 1951¹.

Three main deposits of Ni ores are known—Khalilov, Akermanovka, and Actuba—all have a Ni content of about 2 percent, with the total content of the metal estimated at several hundred thousand tons. Only open-pit mining is used, and the ores are smelted without ore dressing. Only 1 modern plant at Orsk is in operation; 2 other smelters are old and obsolete. The ore is sintered, fluxed to take care of excessive gangue content, and smelted for matte in water-jacketed furnaces. Low Ni content is taken care of by slow descent of the charge and prevention of fines accumulation in the center of the furnaces. About 0.25 percent Ni is lost to the slag. About 350 kilograms of coke per ton of ore produces a matte assaying 30 percent Ni, 20 percent S, and 50 percent Fe. The matte is purified in 5- to 10-ton magnesite-lined converters.

9. BREMHORST, A. Darstellung metallischen Kobalt aus kobalthaltigen Hüttenrückständen [Production of Cobalt Metal From Metallurgical Residues]. Metall u. Erz, vol. 24, 1927, pp. 7-8; Bureau of Mines Inf. Circ. 6331, 1930, p. 29.

10. CANADIAN MINING JOURNAL. The International Nickel Company of Canada, Ltd. Vol. 51, 1930, pp. 1034-1035; Chem. Abs., vol. 25, 1931, p. 267⁶.

Brief outline of development of the Frood property. *General Description*—mines, smelters, and refineries, by Donald MacAskill, pp. 1036-1037. *The Mines*, by Oliver Hall, pp. 1038-1041. These mines furnish $\frac{1}{2}$ of the world's Ni. *The Mill*, by W. T. MacDonald, pp. 1042-1046. Selective flotation discards wastes and makes two smelter feeds. *The Smelter*, by R. M. Coleman, pp. 1047-1052. The smelter units comprise essentially the roasters, the reverberatories, and the converters, with the necessary complementary equipment. Coal-pulverizing plant is a separate small unit. Flow-sheet of the roasting and smelting plant is shown. *The Copper Refinery*, by J. K. Bryan, pp. 1052-1057. Brief description includes an outline, plan, and flow-sheets of the Cu refinery and of the Ag refinery. *Sulfuric Acid and Niter-Cake Plants*, by W. H. DeBlois, pp. 1057-1059. Niter cake is employed in separating Ni and Cu.

11. DRURY, C. W. Cobalt, Its Occurrence, Metallurgy, Uses, and Alloys. Rept. Ontario Bureau of Mines, vol. 27, Pt. 3, 1918, pp. 31-69. Bureau of Mines Inf. Circ. 6331, 1930, p. 5.

An excellent review of various metallurgical methods, including those on getting the cobalt into solution. Metallic cobalt may be obtained by (1) reduction of the oxide in a carbon crucible or by added carbon; (2) reduction of the oxide or oxalate in a stream of hydrogen or hydrocarbons, the reduction being complete at 500°-600° C.; (3) reduction of the oxide by carbon monoxide; (4) reduction of the oxide by ammonium chloride; (5) reduction of cobalt chloride in a current of hydrogen; (6) reduction of the oxide by aluminum (Goldschmidt or thermit process); (7) precipitation from cobalt solutions by metallic magnesium or zinc; (8) distillation of cobalt amalgams; and (9) electrolytic methods.

12. ENGINEERING. The Refinery of the Mond Nickel Company, Ltd., at Clydach, South Wales. Vol. 130, 1930, pp. 349-351, 422-425, and 454-457; Chem. Abs., vol. 25, 1931, p. 57².

13. ENGINEERING AND MINING JOURNAL. The Inco Enterprises. How the Industry Started Fifty Years Ago. Vol. 130, 1930, pp. 426-496; Chem. Abs., vol. 25, 1931, p. 668¹.

Several authors describe the various operations of the International Nickel Co. and its affiliates in the United States and England. Topics discussed include the history of the company, the mines, smelters, concentrators, mills, roasters, blast furnaces, and reverberatory furnaces; sintering of ores; and the refining and uses of nickel and copper, including alloys.

14. GRIFFITHS, W. T. Progress in the Nickel Industry in 1931. The New Canadian Smelter. Metal Ind. (London), vol. 40, 1932, pp. 75-77; Chem. Abs., vol. 26, 1932, p. 1549.

15. GRONNINGSÆTER, A., GILL, J. R., AND MOTT, R. C. Metallurgy at Falconbridge—the World's Newest Copper-Nickel Enterprise. Eng. and Min. Jour., vol. 135, 1934, pp. 195-199; Chem. Abs., vol. 28, 1934, p. 3695⁶.

Describes the plant at the mines of Falconbridge Nickel Mines, Ltd., 13 miles northeast of Sudbury, Ontario.

16. ———. Principles and Practice of Metallurgy at Falconbridge. Trans. Canadian Inst. Min. and Met., 1934 (in Canadian Min. Met. Bull. 264), pp. 219-250; see Chem. Abs., vol. 28, 1934, p. 3695⁶; Chem. Abs., vol. 28, 1934, p. 6661⁹.

Fines go to a sintering plant; coarse fines are low-grade and are used for converter flux. Magnetic sorting and hand picking divide lump into blast-furnace ore and concentrating ore. Bulk flotation of concentrating ore, aiming for low tailings, gives a concentrate which, when added to the direct-smelting ore, forms a self-fluxing mixture with the slag on the basic side. Fines, concentrate, and flue dust are sintered. A blast furnace is used for smelting. Converter slag, as required for flux, is returned to the blast furnace. The flowsheet is described in detail. Lower metal losses

result than by other possible methods. Capital costs are low; only a small flotation plant is needed; the small sintering plant, blast furnace, and converter plant are cheaper than a roasting, reverberatory furnace and converter plant.

17. JOURNAL DU FOUR ÉLECTRIQUE. [Cobalt Recovery at the Union Minière of Upper Katanga.] Vol. 61, January-February 1952, pp. 7-9. Metals Review, vol. 25, No. 6, June 1952, p. 24, item 68-C.

The Co metallurgy in Katanga (Belgian Congo) with respect to development of pyrometallurgical and hydrometallurgical processes is set forth.

18. LIPIN, B. V., AND ZLOKAZOV, N. Y. [Metallurgical Departments of the Ural Nickel Works.] Tsvetnye Metal, No. 6, 1933, pp. 60-74; Chem. Abs., vol. 28, 1934, p. 5009⁹.

Describes works at Verkhni Ufaley (Ural).

19. LYONS, L. A. Australian Metallurgist Reports on African Smelting Progress. Eng. and Min. Jour., vol. 155, No. 1, January 1954, pp. 96-100; Eng. Index, 1954, p. 756.

Reviews the mining industry and metallurgical plants, particularly in the Belgian Congo and Rhodesia. Discusses the smelting methods and data on productions of Sn, Cu, Zn, and Co.

20. MARTHOZ, A. [The Mining and Metallurgical Industry of the Belgian Congo.] Acad. roy. sci. coloniales, Classe sci. tech., Mem. in 8°, vol. 1, No. 1, 1955, 59 pp.; Chem. Abs., vol. 49, 1955, p. 7463d.

Descriptions, with flowsheets, of treatment of Cu-Zn ores from Kipushi, including the recovery of Cd and Ge, of Cu-Co oxide ores and their electrometallurgy, of U-Ra ores, of the extraction of Sn and Au, and the recovery of diamonds. W. Nb, Ta, Bi, and beryl are also recovered.

21. McDIARMID, J. S. Mining in Manitoba. Western Miner, vol. 25, No. 4, April 1952, pp. 80 and 82; Eng. Index, 1952, p. 639.

The following topics are discussed: Expansion of the mineral industry, the value of mineral production, starting production of Ni and Cu at Lynn Lake, exploration work, and oil discoveries.

22. MELCHETT, LORD HENRY MOND. International Nickel Co. Min. Jour. (London), vol. 170, 1930, p. 743; Chem. Abs., vol. 25, 1931, p. 579.

Brief description of various concentrators and refineries of this company in Canada.

23. MINING JOURNAL (LONDON). International Nickel Co. of Canada's Underground Mining Program. Vol. 243, Nos. 6219, 6220, and 6221, Oct. 29, 1954, pp. 486-487; Nov. 5, 1954, pp. 514-517; Nov. 12, 1954, pp. 550-551; Eng. Index, 1954, p. 713.

Discusses geological formation of Sudbury deposits and the conversion to underground mining. The methods of mining vary in the different mines. Gives data on production. Nickel is recovered from pyrrhotite ore. Describes the oxygen flash-smelting process.

24. MINING WORLD. From Africa Comes Cobalt. Vol. 15, No. 12, November 1953, pp. 48-52; Eng. Index, 1954, p. 206; Metals Rev., vol. 27, No. 1, January 1954, p. 36 (11B).

Reviews cobalt deposits, with special reference to the Belgian Congo. Also discusses ores and their mineralogical and chemical composition; open-pit mining; ore preparation, crushing, grinding, classifying, and flotation.

25. RENZONI, L. S. Metallurgical Research in Canada. Canadian Min. and Met. Bull., vol. 45, No. 480, April 1952, pp. 217-223; Eng. Index, 1952, p. 605.

Discusses Cu, Ni, and Co.

26. RICKARD, T. A. The Nickel of Sudbury. Canadian Min. Jour., vol. 63, 1942, pp. 785-792; Chem. Abs., vol. 37, 1943, p. 856⁴.

Presents story of the Canadian properties of the International Nickel Co. Cites 21 references.

27. ROGER, E. [Metallurgy of Copper and Cobalt at Katanga.] Congr. internat. mines mét. géol. appl., Met. sec., 6th sess., Liège, June 1930, pp. 441-456; Metals and Alloys, vol. 3, abs. 52; Chem. Abs., vol. 26, 1932, p. 4279.

Recounts an unsuccessful experience with water-jacketed furnaces. The oxidized Cu ores are subjected to gravity concentration and flotation, and the finely divided product is smelted in reverberatories. Lean ores are leached, and the metal is recovered by electrolysis. Flowsheets are given and many details described. Co-bearing ores are smelted in water-jacketed furnaces, the Cu being reduced and the Co and Fe being left in the scoria, which passes to electric smelting furnaces. High-Co ores are subjected directly to electric smelting. The smelting process produces an alloy of Cu-Co-Fe which liquates into two separable products—a red alloy of Cu 90-93 percent, Co 3-5 percent, and Fe 3-5 percent and a white alloy of Cu 14-17 percent, Co 34-35 percent, and Fe 35-45 percent. The process is regulated to produce as much of the white alloy as possible, since recovery of Co from it is easier than from the red alloy.

28. ROWE, R. C. Elements of Progress. (STANLEY, R. C.—Foreword.) International Nickel Co. of Canada. Canadian Min. Jour., vol. 67, No. 5, May 1946, pp. 305-356. Feature issue supplementing similar symposium as indexed in Eng. Index, 1937, p. 770, from issue of November 1937. Eng. Index, 1946, p. 753.

Rowe discusses the International Nickel Co. and its affiliates in the United States and England with regard to geology, mining, milling, smelting, Cu refining, Ni refining, Horseshoe Lake, power, technical control, transportation, designing, maintenance, purchasing, stores, and fire protection in Canada in part I. Parts II, III, IV, and V detail industrial relations practices, United States operations, United Kingdom operations, and world markets, respectively.

29. SAVELSBERG, W. [Physical Chemistry in Metallurgical Operations.] Ztschr. Elektrochem., vol. 43, 1937, pp. 474-479; Chem. Abs., vol. 33, 1939, p. 8153⁹.

Describes purification of the electrolyte in the recovery of Zn, Cu, and Ni from their ores, the mechanism of liquation, the partition of metals between slag and matte or between two matte layers, the Harris Pb-refining process, the reduction of SnO₂ to Sn by CO, and the purification of metals on the converter principle.

30. SENGIER, E. B. Katanga's Mineral Empire Based on Many Metals. Eng. and Min. Jour., vol. 152, November 1952, pp. 86-89; December 1951, pp. 92-96; Metals Rev., vol. 25, No. 1, January 1952, p. 20 (17B); Chem. Abs., vol. 46, 1952, p. 1931b.

This central African enterprise yields Cu, Zn, Co, Cd, Au, and Ag. Operations comprise open-pit and underground mining, concentration, smelting, and electro-winning. November installment describes deposits, mining procedures and production, and gives labor-productivity data. December installment discusses gravity concentration, flotation, smelting, leaching, and electrolytic recovery.

31. SEVIN, R. [The Metallurgy and Electrometallurgy of Cobalt.] Jour. du four élec., vol. 36, 1927, pp. 17-19; Chem. Abs., vol. 21, May 10, 1927, p. 1412; Bureau of Mines Inf. Circ. 6331, p. 33.

32. SHERIDAN, L. M. The New Smelter and Concentrator of the International Nickel Co. at Copper

Cliff, Ontario. Eng. Jour. (Canada), vol. 13, 1930, pp. 682-687; Chem. Abs., vol. 25, 1931, p. 1472².

After coarse crushing at the mines, the ore is shipped to Copper Cliff, where it is crushed to 200-mesh and sent through a wet-concentration process to remove the rock. In the concentration process the sulfides are floated. By selective flotation a rough separation is made of the Cu and Ni. Smelting comprises roasting in multiple-hearth roasters, in reverberatory furnaces and blowing in basic-lined Bessemer converters. The product is an 80 percent Cu-Ni matte. The layout of the smelter and concentrator is shown in a diagram.

PRINCIPLES AND PROCESSES

33. ABEGG, R., AUERBACH, F., AND KOPPEL, I. Handbuch der anorganischen Chemie. Bd. IV, Abt. 3. Die Elemente der 8 Gruppe des periodischen Systems. Tl. 3, Kobalt; Lfg. 1, S. Hirzel Leipzig, about 760 pp. [Handbook of Inorganic Chemistry, vol. 4, section 3. The Elements of the Eighth Group of the Periodic System. Part 3, Cobalt, No. 1.] (See Chem. Abs., vol. 27, 1933, p. 678); Chem. Abs., vol. 28, 1934, p. 726³.

34. ANAZAWA, KENJI (Furukawa Research Lab.). [Metallurgy of Nickel.] Jour. Electrochem. Soc., Japan, vol. 16, 1948, pp. 100-105; Chem. Abs., vol. 44, 1950, p. 9314e.

Describes industrial processes for the metallurgy of Ni used during the war: (a) Production of raw Ni from arsenide or Ni ores (10 percent); (b) from the byproducts of Pb and Zn metallurgy in Burma; (c) electrolytic separation of Ni and Co; (d) manufacture of extra-pure Ni; and (e) recovery of Ni from lean Japanese ores.

35. BAILEY, A. R. Nickel Production. Metal Ind., vol. 84, No. 2, Jan. 8, 1954, pp. 23-24; Eng. Index, 1954, p. 713; Chem. Abs., vol. 48, 1954, p. 4398h; Metals Rev., vol. 27, No. 3, March 1954, p. 25 (41c).

Discussed are: Current developments in refining processes; treatment of Sudbury ores at International Nickel Co. plant at Copper Cliff, Canada; smelting of Ni concentrate; the Orford process employed for separating Cu and Ni sulfides. A new process, the details of which have not been given, will make it possible to obtain extremely high grades of Fe ore in addition to Ni. A new pressure-leaching process will deal with sulfide ore without any previous roasting or reduction. Bibliography is included.

36. BARTH, OTTO. [Modern Nickel Metallurgy.] Tek. Ukeblad, vol. 90, 1943, pp. 100-101; Chem. Zentralb., vol. I, 1944, p. 473; Chem. Abs., vol. 39, 1945, p. 1612⁵.

A review of the development of methods of treatment of Cu-free and for Cu-containing Ni ores, covering electrolytic and chemical processes, the direct treatment by the Mond and the Krupp processes, and Ni deposits in Finland.

37. BEALL, JOHN. Cobalt Review. Min. Eng., vol. 190, 1951, pp. 17-24; Chem. Abs., vol. 45, 1951, p. 1933e.

Gives production, consumption, and uses of Co as well as the efficiency of Co in various magnetic alloys. Tests compositions of 13-65 percent Co high-temperature alloys, along with names and locations of domestic refiners and processors. Includes flowsheet which outlines the steps taken to recover Co from pyrites.

38. BERG, GEORG, AND FRIEDENSBURG, FERDINAND. Metallischen Rohstoffe, vol. VI, Nickel und Kobalt, J. W. Edwards Co., Ann Arbor, Mich., 1947, 288 pp.; Chem. Abs., vol. 42, 1948, p. 1178e.

39. BRUNO, WAESER. [Progress in the Inorganic Heavy-Chemical Industry. XIV. Heavy-Metal Compounds and Others—Conclusion.] Chem. Fabrik.,

vol. 14, 1941, pp. 248-255. See Chem. Abs., vol. 35, 1941, p. 4922⁷; Chem. Abs., vol. 38, 1944, p. 5369¹.

Reviews 943 patents and papers between 1933 and December 31, 1940, on compounds of Ni and Co, among many other metals, with many references.

40. CHALLANSONNET, JEAN. [Cobalt.] Tech. moderne, vol. 30, 1938, pp. 483-489 and 539-541; Chem. Abs., vol. 35, 1941, p. 3202⁴.

The occurrence, methods of extraction, physical and mechanical properties, and chemical and magnetic data are reported for Co. The properties of alloys of Co with Fe, in high-speed steel, and with Ni, Cr, Cu, and Co-Cu-Be were determined. The Co-Cu-Be alloy shows valuable properties in electric manufacture.

41. COHEN, G. Le cuivre et le nickel. Paris. Presses Univ. France, 1952, 128 pp.; Chem. Abs., vol. 47, 1953, p. 6330f.

42. DEAN, R. S. The Metallurgical Research Program of the Bureau of Mines (Washington, D. C.) Relating to Iron and Steel. Bureau of Mines Rept. of Investigations 3920, 17 pp.; Chem. Abs., vol. 40, 1946, p. 5681⁴.

Fifteen years of research is summarized in the field of Fe and ferroalloys of Co, Ni, Cr, and Mn. The production of pure metals for alloying and the more efficient methods for utilizing low-grade domestic ores are reviewed. Some headings are: Fe ore concentration; agglomeration of Fe ores and reproducibility; direct reduction of Fe ore; special refining processes; pure Mn; pure Cr; Co; production of ferro-nickel and ferrocobalt from domestic ores; and development of special alloys. By adjusting the technology, the Bureau has found ways of utilizing low-grade ores to produce pure metals and to produce alloys frequently superior to those made by orthodox methods from high-grade ores.

43. DEAN, R. S., AND SILKES, B. Metallurgical Research Program of the Bureau of Mines Relating to the Nonferrous Metals. Bureau of Mines Rept. of Investigations 4064, 1947, 22 pp.; Chem. Abs., vol. 41, 1947, p. 5065i.

Reviews and bibliographies of Bureau of Mines papers relating to ore-dressing, natural-gas reduction of Zn, Scotch-hearth melting of Pb, electrolytic Sb recovery of Ni from Ni, Cr, Fe ore, Al and Mg. Al and Mg alloys, ductile Ti, and electrolytic Co, Cr, Mn and their alloys.

44. DENNIS, W. H. The Metallurgy of Cobalt. Min. Mag., vol. 81, Nos. 3 and 4, September 1949, pp. 144-148; October 1949, pp. 215-218; Chem. Abs., vol. 44, 1950, p. 986c.

Discusses early sources and production of Co; recovery of Co from Cu ores, from cobaltiferous arsenical ores, and from speiss; extraction from pyrite; Co occurrence in New Caledonia; uses of Co; Co alloys; magnets; and cutting tools.

45. ———. Nickel Smelting and Recovery. Min. Mag., vol. 70, 1944, pp. 137-144; Chem. Abs., vol. 38, 1944, p. 3228⁵.

A general review.

46. DISMANT, J. H. Review of Cobalt-Metal Production—Notes on Literature. Mines Mag., vol. 62, January 1952, pp. 21-23 and 44; Metals Rev., vol. 25, No. 4, April 1952, p. 17, item 100-B.

The discussion includes uses in the ceramic and metallurgical industries as well as processes for the recovery of Co from roasted pyrites.

47. DOWNIE, C. C. Present-Day Blast Smelting of Nickel. Metal Ind. (London), vol. 45, 1934, pp. 195-197; Chem. Abs., vol. 28, 1934, p. 6668.

48. DOWNIE, C. C. Engineering Features of Nickel Smeltery. *Min. Jour.* (London), vol. 239, No. 6110, Sept. 26, 1952, pp. 342-343; *Eng. Index*, 1952, p. 675.

The smeltery layout, with its equipment such as furnace downtakes, stacks, and foundations, is shown, and the smelting is discussed. Safety precautions are set forth.

49. ———. Practical Notes on Smelting Nickel Ores. *Min. Jour.* (London), vol. 239, No. 6123, Dec. 26, 1952, pp. 738-739; *Eng. Index*, 1953, p. 704.

The efficiencies of electric-hearth and blast-furnace practices are compared. Constructional details in connection with air blasts are given. It is concluded that, provided reliable air-blast conditions exist and straight runs of the same briquets are used, the total cost of the air blast remains less than those incurred by electric smelting.

50. DRURY, C. W. Cobalt. *Mineral Ind.*, vol. 42, 1933, pp. 108-112; *Chem. Abs.*, vol. 28, 1934, p. 7215⁷.

Discusses production, trade, metallurgy, uses, and statistics. Bibliography is appended.

51. DYSON, G. M. The Extraction and Utilization of Cobalt. *Chem. Age*, vol. 19, No. 488, *Met. Sec.* pp. 33-35, and No. 492, *Met. Sec.* pp. 41-42, 1928; *Chem. Abs.*, vol. 23, 1929, p. 799⁹.

There are three main types of material for the manufacture of Co; (1) High-grade Co materials (for example, the Cloncurry deposits of Queensland, averaging 20 percent of this element); (2) the residues from the Mond process for the extraction of Ni, containing Co, much Fe, and very little Ni; and (3) byproducts from the extraction of Au and Cu in certain Canadian minerals, the residues containing approximately 8 percent Co and 6.6 percent Ni and the speiss 17.5 percent Co and 19 percent Ni. The residues or minerals are smelted in a low-pressure blast furnace or cupola, with the addition of various slagmaking materials; the As and S combine with the Fe, Ni, and Co present, forming a heavy speiss. The speiss, finely ground and calcined in a mechanically stirred rabbling furnace, has much of its As volatilized as As_2O_3 . Further treatment is almost purely chemical and involves two stages: (1) Removal of the residual As and (2) separation of Co from Ni. The ground speiss is treated with HCl and enough $FeCl_3$ to convert the As to ferric arsenate, which is thrown out of solution by the addition of milk of lime and H_2S . Enough $CaOCl_2$ is added to the clear solution after the removal of As, Fe, and Cu to precipitate the Co as the hydrated oxide. Co metal may be obtained by smelting the oxide with charcoal in a small blast furnace. The electrical properties of Co steels are eminently suitable for the manufacture of magneto magnets. Other uses are mentioned.

52. ENGINEERING AND MINING JOURNAL. Nonferrous Metallurgy. Vol. 153, No. 2, February 1952, pp. 131-133; *Eng. Index*, 1952, p. 605.

Reviews progress in the methods of production of nonferrous metals, hydrometallurgy, a separation process for Ni and Cu, Ti production, and work on Zr. Describes a process in which an ammonia solution and oxygen effect dissolution of a nickel concentrate, yielding Ni and Co metal by hydrogen reduction without pyrometallurgy.

53. FRIEND, J. N. The Chemistry of Cobalt. *Textbook of Inorganic Chemistry*, vol. 9, part I, 1919, pp. 19-77.

Gives details on a very large number of Co compounds and complexes.

54. ———. The Historical and Industrial Discovery of the Elements. VII. Cobalt, Nickel and Platinum Metals. *Chem. and Ind.*, 1941, pp. 643-647 (*see*

Chem. Abs., vol. 35, 1941, p. 3491⁹); *Chem. Abs.*, vol. 35, 1941, p. 7772⁸.

55. GIBSON, T. W. Nickel. *Mineral Ind.*, vol. 43, 1934, pp. 421-428; *Chem. Abs.*, vol. 29, 1935, p. 7241⁶.

Discusses Canadian and other deposits of Ni, gives data on production, uses of Ni, and notes on technical development.

56. GMELIN'S HANDBUCH DER ANORGANISCHEN CHEMIE. System-Nr. 58, Kobalt. Ed. by Deutschen chemischen Gesellschaft, 8th ed.; *Tl. A. Lfg. 2*, 282 pp. M. 48 (*see Chem. Abs.*, vol. 25, 1931, p. 658); *Chem. Abs.*, vol. 26, 1932, p. 4766.

57. GREENWOOD, H. W. Metal Supplies and Powder Metallurgy Tomorrow. *Metallurgia*, vol. 49, No. 293, March 1954, pp. 135-136; *Eng. Index*, 1954, p. 757.

Presents hydrometallurgical and exchange methods of extracting and separating lower grade materials. Ni, Cu, and Co are separated by a flotation process. Ion exchange recovers metals from dilute solutions and is applied to U extraction. It is stressed that in certain processes metal powders suitable for use in powder metallurgy are produced.

58. GUILLET, LEON. [Recent Advances and Economic Situation of Metallurgies Other Than Ferrous. V. Nickel.] *Rev. mét.*, vol. 32, 1935, pp. 321-341; *Chem. Abs.*, vol. 29, 1935, p. 7892⁶.

Discusses present metallurgical practices and refining methods of Ni plants in Canada, Wales, Norway, and New Caledonia. Canadian installations include facilities for producing raw metal, and also refining plants; in Wales and Norway are refining plants and at New Caledonia mining and smelting to mattes.

59. HOWAT, D. D. Nickel. *Mine and Quarry Eng.*, vol. 6, 1941, pp. 291-295 and 308; vol. 7, 1942, pp. 11-13; *Chem. Abs.*, vol. 36, 1942, p. 2504¹.

Describes mining, metallurgy, and refining of Ni.

60. HUGONY, E. Il nichelio [Nickel]. *Industria*, vol. 55, No. 2, February 1941, pp. 27-33; *Eng. Index*, 1948, p. 831.

Historical survey, dealing with the metallurgy, properties, alloys, uses, and economic situation of Ni.

61. INTERNATIONAL NICKEL Co. (New York). Development and Research Division. Nickel and Nickel Alloys (looseleaf book); *Chem. Abs.*, vol. 37, 1943, p. 597⁶.

The alloys of nickel with Fe, Cu, and other metals have many desirable properties. The winning of Ni from its source materials is not stressed.

62. JEFFRIES, ZAY. Review of Rare and Precious Metals. *Min. and Met.*, vol. 23, 1942, pp. 69-70 (*see Chem. Abs.*, vol. 35, 1941, p. 3574⁹); *Chem. Abs.*, vol. 36, 1942, p. 1575⁹.

Refined Co, formerly from Belgium, is now supplied by the United States and Canada. The use of Ag is increasing. In some civilian applications it is replacing Ni and other metals. The status of many metals is reviewed.

63. JOHNSTONE, S. J. Minerals for Chemical and Allied Industries; Review of Sources, Uses, and Specifications, XV. *Ind. Chem.*, vol. 23, 1947, pp. 794-800; *British Abs.*, 1948, p. B-1-493.

Discusses the ore deposits and metallurgy of Ni and the uses of Ni in special steels and other alloys, in electroplating, as a catalyst in hydrogenation, in vitreous enamels, and in alkaline storage batteries.

64. KOELSCH, —. [Lung Cancer and Occupation.] *Acta Unio Intern. Contra Cancrum* (Paris), vol. 3, 1938, p. 243; *Zentralb. Gewerbehyg. Unfallverhüt.*, vol. 27, 1940, pp. 32-33; *Chem. Abs.*, vol. 35, 1941, p. 3732⁶.

All occupational dusts or vapors inhaled do not cause lung carcinoma; the effects of various named dusts are

discussed, also tar and tobacco smoke; there have been a number of cancers in workers on Ni ores.

65. KROLL, W. J. German Metallurgy in Wartime, parts I and II. Eng. and Min. Jour., vol. 144, 1943, No. 9, pp. 50-51; No. 10, pp. 82-83 and 104; Chem. Abs., vol. 38, 1944, p. 41⁹.

Considers Ni, Mg, Zn, and rare metals from the viewpoint of winning them from various scrap sources or from ores.

66. McLAREN, D. C. Cobalt, Its Occurrence, Chemistry, Use, and Metallurgy. Canadian Min. Jour., vol. 64, 1943, pp. 341-350; Chem. Abs., vol. 37, 1943, p. 4828⁴.

Review.

67. MELLOR, J. W. Nickel. A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. 15, 1935, pp. 1-497.

As the title of the book states, this discussion is quite comprehensive and covers such topics as history, occurrence, extraction, and preparation of nickel and uses as catalyst, physical and chemical properties, atomic weight and valence, intermetallic compounds, and compounds of the element.

Extraction of Nickel, work cited above, pp. 15-33. The general procedure in dealing with a sulfide ore involves roasting the ore, smelting to a regulus or matte, enriching the matte, and converting the enriched matte into crude metal.

Arsenical ores are now very little worked. The ore, freed from gangue, was first roasted to remove some of the arsenic. Nearly all the iron can be oxidized and slagged before the nickel arsenide is attacked. This produces a crude speiss, which is enriched by a second fusion. The roasted charge, mixed with carbon, is strongly heated to reduce to arsenides, from which the arsenic is removed by heating with niter and soda, followed by leaching with water. Nickel oxide is produced.

Oxidized Ni ores, such as garnierites, have been smelted with suitable fluxes and reductants to ferro-nickel; however, the process was unsatisfactory. It was found preferable to smelt the ore in a blast furnace with addition of S to form a regulus or matte, which is then treated further to recover the metal. Wet processes for extracting Ni from its ores are regarded as generally unsatisfactory.

The electrolytic extraction of Ni directly from its ores has not been successful; however, electrolytic methods can successfully recover nickel from mattes or other metallurgical products rich in Ni. Ni can be refined electrolytically or by dry processes.

Mellor includes a very extensive bibliography.

68. ———. Cobalt. A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. 14, 1935, pp. 419-859.

The history, occurrence, extraction, separation of Co from Ni, preparation of metal, physical properties, chemical properties, atomic weight and valence of Co, and a very extensive list of Co compounds and complexes are covered very thoroughly.

Extraction of Cobalt, work cited above, pp. 433-440. A multitude of processes has been used. In some instances byproduct Co is recovered, with precious metals or Mn; in others it is recovered alone. The three main types of ores are arsenical, sulfides, and oxidized. For arsenical ores processes include smelting to a speiss, chloridized roasting of the speiss, extraction with water, purification of the solution, precipitation of a cobalt salt, and calcination. In another process the ore is fused with potassium carbonate and S. After leaching with water, impure cobalt sulfide is separated and further purified. Several other processes are mentioned. Sulfide ores can be roasted alone, with silica or silicates,

with polysulfides, sulfates, carbon, and silica, bessemerized with limestone, or smelted with barium sulfate and silica. Sulfate roasting, oxidation with steam under pressure, heating with alkali chloride, sulfate, sulfide, and calcium carbonate have also been used. After the oxide is obtained (or sulfide in a relatively pure state) it may be smelted to metal with carbon. For oxidized ores some workers melt the ore with suitable fluxes to slag off the iron. In other processes, a partial reduction acts selectively to reduce Cu, leaving Co in the slag. The slag, mixed with lime and carbon and heated electrically, produces an alloy containing Co, Cu, Fe, and Si, which is purified further. Other workers heated the ore with carbon and lime or with carbon and calcium sulfate.

Leaching. Leaching can be performed either on the raw concentrates or on roasted materials. The ores may be roasted alone or with salts or gases to open them up, after which either acids alone or combinations of acids and salts, such as those of Fe, Mg, or Na, are employed to dissolve the metal or combined Co. A speiss or regulus can be dissolved by making it the anode in an electrolysis circuit. Electrolysis may be regulated to separate Co and Ni.

The Separation of Cobalt and Nickel, work cited above, pp. 440-445. Numerous separation schemes (31) are outlined. They are based upon preferential solution of salts, fractional precipitation, fractional crystallization, selective solvent extraction, selective carbonyl formation, and other processes. Long list of references.

69. MEYER, R. J. Gmelin's Handbuch der anorganischen Chemie. 8th ed. Iss. by Deutsche chemische Gesell. System-Nr. 59. Eisen. Tl. B. Lfg. 3, 143 pp. System-Nr. 26. Beryllium. 180 pp. System-Nr. 58. Cobalt. Tl. B. The Cobaltamines. 376 pp. Berlin: Verlag Chemie, G. m. b. H. Reviewed in Jour. Am. Chem. Soc., vol. 52, 1930, pp. 4614-4615 (see Chem. Abs., vol. 24, 1930, p. 3192); Chem. Abs., vol. 25, 1931, p. 658.

70. MINING JOURNAL (LONDON). The Free World's Nickel-Refining Troubles. Vol. 242, Jan. 29, 1954, pp. 124-125; Metals Rev., vol. 27, No. 4, April 1954, p. 34, item 53-C.

Reviews history of the Ni industry. Ni-refining facilities, engineered to meet local conditions, will be erected both on the North American Continent and in Cuba.

71. MOND, ROBERT. [The Evolution of the Nickel Industry.] Chim. et ind., vol. 38, 1937, pp. 835-839; Chem. Abs., vol. 32, 1938, p. 2880⁷.

72. MORE, C. H. [Cobalt and Its Compounds.] L'Argile, No. 177, 1937, pp. 9-13; Chem. Abs., vol. 32, 1938, p. 2043⁴.

More describes in detail various deposits of Co, its compounds, and their characteristics. Co is used extensively in the ceramic industry as a pigment for obtaining blue, pink, red, green, and yellow.

73. NATIONAL BUREAU OF STANDARDS. Nickel and Its Alloys. Circ. 485, 1950, pp. 1-4 and 68-72; Chem. Abs., vol. 44, 1950, p. 5299b.

Gives a short résumé of the various world sources of Ni, showing Canada leading with about 85 percent of the world production, followed by the U. S. S. R., Cuba, New Caledonia, Norway, and Finland. Several methods of Ni extraction, including the Orford, the Hybnette, and the matte process of New Caledonia are mentioned. (402 refs.)

74. NATIONAL SECURITY RESOURCES BOARD, MATERIALS OFFICE (Bureau of Mines and Geological Survey). Nickel. 1950 Materials Survey, April 1952, 16 chapters, pagged separately; Eng. Index, 1952, p. 674.

History of world production; commercial forms and uses; minerals, ores, and geology; reserves, by coun-

tries; economics of Ni ores; mining, milling, and metallurgy; marketing; data on production, imports, exports, stocks, and consumption; conservation and substitutes; present and planned facilities for developing Ni industry; Government control; maps, diagrams. Short bibliography.

Chapter VII. Mining, milling, and metallurgy. Several processes in use are reviewed under titles: Inco Process Before 1948, Orford Process, Effect of Copper and Precious Metals, New Inco Process, Falconbridge Hybinette Process, New Caledonia Process, Mond Process, German Modification of Mond Process, Mond Process, Krupp-Renn Process, Caron Ammonia Leach Process, Other Potential Processes, Alsifer Process, Cuban Nickeliferous Iron Ores.

75. NATIONAL SECURITY RESOURCES BOARD, MATERIALS OFFICE. (Bureau of Mines and Geological Survey). *General Metallurgy of Cobalt.* Materials Survey: Cobalt, 1952, chap. V, pp. V1-V30.

The metallurgy of Co involves many operations: Ore dressing, electric furnacing, converting, reduction, smelting to speisses, electrowinning, and purification, many of which are practiced at the various localities cited in the report. Flowsheets are given for the Belgian Congo; Nkana, Northern Rhodesia; Bou-Azzer, French Morocco; for refining Rhokana alloy in Canadian and Belgian refineries; for refining in Wilmington, Del.; for electrolytic Co production in Belgian Congo; and for the Blackbird mine, Forney, Idaho. Includes a bibliography.

76. NEGRU, J. S. (International Nickel Co.). Literature and Patent References to Nickel. Pub. February, 1930, 51 pp.; March, 54 pp.; and April, 62 pp.; Chem. Abs., vol. 24, 1930, p. 3743².

Includes bibliography on Ni, Ni alloys, Ni steels, and Ni cast irons.

77. PARSONS, C. L. Production of Nickel and Cobalt. Notes on Mineral Wastes. Bureau of Mines Bull. 47, 1912, pp. 17-18.

78. PEREL'MAN, F. M., ZVORYKIN, A. YA., AND GUDIMA, N. V. Kobalt [Cobalt]. Moscow, Akad. Nauk S. S. S. R., 1949, 173 pp.; Chem. Abs., vol. 47, 1953; p. 4273d.

79. PERRAULT, R. Le Cobalt (preface by P. Chevenard). Dunod, Paris, 1946, 151 pp., illus. diagrams, charts, tables; Eng. Index, 1947, p. 236.

The book includes a brief history of Co and its early uses; minerals containing Co; the location and nature of important deposits; processes for concentration and extraction, including an electrolytic method; mechanical and chemical properties; survey of applications, including uses of its oxides and salts; production and consumption figures.

80. RAUDEBAUGH, R. J. Nonferrous Physical Metallurgy (chapter on Nickel); Pitman Publishing Corp., New York, N. Y., 1952, 345 pp.; Eng. Index, 1953, p. 707.

Emphasis is placed on recent developments in processing, fabrication, and applications. A special chapter covers powder metallurgy and refractory metal composites.

81. ROBIETTE, A. G. E. Electric Smelting of Nonferrous Metals. Metal Ind. (London), vol. 83, 1953, pp. 161-165; Chem. Abs., vol. 47, 1953, p. 12057e.

Reviews methods, equipment, and raw materials used in the electric smelting of Ni, Cu, Sn, Pb, Zn, Al, and Mg.

82. ROYAL ONTARIO NICKEL COMMISSION. Report on Nickel Ores, Smelting, Refining of Nickel From Canada and Other Localities. A. T. Wilgress, Toronto, Canada, 1917, 584 pp. (with appendix, Smelting and Refining Processes, 219 pp.), pp. 424-486.

The Mond process, with its Ni carbonyl formation

and subsequent decomposition into carbon monoxide with Ni metal deposition, is described in detail. The Orford process depends upon the separation of "tops" and "bottoms"; the sulfides of metals dissolved in sodium sulfide separate quite sharply with Ni in the "bottoms" and copper in the "tops", when the liquid sulfides are poured into suitable containers. The Hybinette process, primarily electrolytic, is also described. The ores, together with their metallurgy are detailed for New Caledonia, Cuba, Norway, and other countries. A chapter on the chemistry of Ni is included.

83. SCARLOTT, C. A. Present and Future of Nickel and Cobalt. Materials and Methods, vol. 34, No. 1, 1951, pp. 61-65; British Abs., 1952, p. B-1-239.

Briefly reviews production and applications of Ni, Co, and their alloys.

84. ———. The Story of Nickel and Cobalt. Westinghouse Eng., vol. 11, 1951, pp. 117-123; Chem. Abs., vol. 45, 1951, p. 10153i.

Presents origin, mining, recovery, uses, economics, history, and political implications of Ni and Co.

85. SCHLECHT, HELMUT, AND SCHLECHT, LEO (assigned to I. G. Farbenindustrie, A. G.). [Recovery of Copper and Nickel From Their Ore.] German Patent 699,450, Oct. 31, 1940 (Cl. 40a, 43.01). See United States Patent 239,626, Chem. Abs., vol. 35, 1941, p. 4721¹; Chem. Abs., vol. 35, 1941, p. 6913⁶.

86. SCHLECHTEN, A. W., AND HANLEY, H. R. In Metallurgy, the Accent Is on New Metals, New Methods. A Review. Missouri Sch. Mines, Rolla, Mo.; Eng. and Min. Jour., vol. 152, No. 2, 1951, pp. 122-125, 183; Chem. Abs., vol. 45, 1951, p. 3307d.

Considers Ti, V, Zn, Mo, Cr, Si, Cu, and Pb matte from slag, hearth melting at Trepica, Zn, Ni, Co, and Al.

87. STANLEY, R. C. Nickel—Past and Present. Trans. Canadian Inst. Min. and Met., 1935 (in Canadian Min. and Met. Bull. 277), pp. 176-208; Chem. Abs., vol. 29, 1935, p. 5389⁹; Min. Jour. Centenary, 1935, p. 44; Chem. Abs., vol. 29, 1935, p. 5390⁹.

Discusses the main uses for Ni, its employment in 131 alloy steels and 63 other alloys, together with early metallurgical and refining methods.

88. TAFEL, VICTOR. Lehrbuch der Metallhüttenkunde, Bd. II, Wismut, Blei, Zinn, Antimon, Zink, Quecksilber, Nickel, Aluminium. [Textbook of Metallurgy, vol. II, Bismuth, Lead, Tin, Antimony, Zinc, Mercury, Nickel, Aluminium.] S. Hirzel, Leipzig, Germany, 671 pp.; Chem. Abs., vol. 23, 1929, p. 5147.

89. ———. [Metal-Smelting Methods in the Year 1930.] Metall. u. Erz., vol. 28, 1931, pp. 503-510; Chem. Abs., vol. 26, 1932, p. 673.

Reviews methods applied to the smelting of Pt, Au, Ag, Cu, Pb, Sn, Sb, Zn, Cd, Hg, Ni, and Al.

90. ———. [Smelting in the Years 1937 and 1938.] Metall. u. Erz., vol. 36, 1939, pp. 384-389, 415-419, 441-448, 484-491, 504-507, 516-522, and 532-541; Chem. Abs., vol. 34, 1940, p. 1284⁸.

Describes smelting methods for various nonferrous metals, including Ni and Co. Electrolytic, as well as dry and wet methods, and ore dressing are discussed.

91. ———. [Smelting Methods in the Years 1934 to 1936.] Metall. u. Erz., vol. 34, 1937, pp. 340-348 and 372-381 (see Chem. Abs., vol. 31, 1937, p. 6160⁹); Chem. Abs., vol. 31, 1937, p. 7805⁸.

Describes smelting of Hg, Ni, Co, Al, Mg ores and the refining of the crude metals.

92. TSEIDLER, A. A. [History of Nickel Metallurgy.] Tsvetnye Metal, 1930, pp. 744-751; Chem. Abs., vol. 26, 1932, p. 5520.

93. TSEIDLER, A. A. [Ferrous and Nonferrous Metallurgy.] *Metallurgiya Nickelya*, Moscow, Sci. Tech. Pub. House, 1947, 314 pp.; Chem. Abs., vol. 43, 1949, p. 2566b.
94. TYLER, P. M. Cobalt. Bureau of Mines Inf. Circ. 6331, 1930, 33 pp.
Topic headings are: Introduction, description, uses, mode of occurrence, identification, metallurgy, world production, domestic production and deposits, imports and exports, the industry in foreign countries (Australia, Belgian Congo, Canada, New Caledonia, South Africa), market grades, prices, North American buyers, British buyers, bibliography.
95. WADHAMS, A. J. The Story of the Nickel Industry. *Metals and Alloys*, vol. 2, 1931, pp. 166-175; Chem. Abs., vol. 26, 1932, p. 54.
96. WALTER, H. W. Nickel—Its History, Refining, and Uses. *Canadian Chem. Met.*, vol. 15, 1931, pp. 185-191; Chem. Abs., vol. 25, 1931, p. 4498².
Discusses sources of Ni, smelting operations at Copper Cliff, refining from Bessemer matte, and Mond and Hybinette processes. Charts show the flowsheet of operations at the Port Colborne refinery, and the flowsheet showing the flow and purification of electrolyte. Describes uses.
97. WELLS, R. C. Relative Abundance of Nickel in the Earth's Crust. *Geol. Survey Prof. Paper*, vol. 205-A, 1943, pp. 1-21; Chem. Abs., vol. 38, 1944, p. 9374.
Nickel was determined in all types of rocks and found to be most abundant in ferromagnesian rocks. It was also present in shales, silts, and clays. A reasonable estimate in the 10 miles depth of the earth's crust is 0.016 percent Ni. Gives methods of analysis.
98. WRIGHT, W. G. Story of Nickel Since 1939. *Australasian Eng.*, vol. 45, March 1953, pp. 42-50; Eng. Index, 1953, p. 703.
An account of the activities of the International Nickel Co. since 1939. Describes sources of Ni in Finland, Cuba, Brazil, Celebes, Caledonia, and Canada with improvements in refining and further information.
99. YOUNG, R. S. Cobalt. *Am. Chem. Soc. Mon.* 108, Reinhold Publishing Corp., New York, N. Y., 1948, 181 pp. (illus., charts, maps, tables); Eng. Index, 1949, p. 219.
Assembles and critically reviews existing data on chemistry and metallurgy of Co; certain unpublished features and developments that have come within the author's experience are included. Promising lines for further investigation in various fields are indicated.

OXIDIZED ORES

100. CHIZHIKOV, D. M. [First Soviet Nickel.] *Tsvetnye Metal*, No. 6, 1933, pp. 3-16; Chem. Abs., vol. 28, 1934, p. 4688⁹.
Describes the first Soviet Ni plant, at Ufalet, Urals. The ore supply comes from the oxidized Ni ore deposits in the vicinity of the works with an average Ni content of 2 percent. The proved ore contains 16,000 tons of Ni. It is intended to smelt the ore into an Fe-Ni matte and to separate and refine the Ni. Describes the approved metallurgical processes, furnaces, and ore-mining conditions. The plant was to be put in operation during the winter of 1933.
101. DHAVERNAS, J. [French Nickel. History of the Exploitation of New Caledonian Ore.] *Rev. nickel*, vol. 8, 1937, pp. 70-75; Chem. Abs., vol. 31, 1937, p. 5727⁶.
102. DOUGHERTY, R. S. A. (assigned to Bethlehem Steel Co.). Ore Preparation. U. S. Patent 2,717,829, Sept.

13, 1955. (Notes of O. C. Ralston, Bureau of Mines, Washington, D. C.)

This patent application was filed Oct. 17, 1950, and is the earliest disclosure of Bethlehem's style of thinking, which has been greatly simplified and changed since 1950. It is written entirely on Mayari (Cuba) laterite, except that the claims are broader and all of them merely mention ferrous ores containing nickel.

In 1950 everyone was interested in pressure digestions à la Chemical Construction Co. Dougherty still prerduced the ore but did his leaching under elevated temperature and pressure. Precipitation was accomplished in an autoclave.

The reduction step is not described in detail, but presumably gas reduction is involved to the point where all the nickel and cobalt were in the metallic condition. The Fe was also partly reduced to metal, but with no upper limit. Tests on ore with 70-80 percent of the Fe in the form of sponge have been just as successful in leaching as those with only 2-3 percent metallic Fe.

The autoclave leach involved pumping in an aqueous solution with 18 percent ammonium carbonate, which alone will not take Ni and Co into solution, but after closing, the cold autoclave ammonia was pumped into at least 9 percent by weight of the solution, together with oxygen gas, making the total cold pressure 200 p. s. i. The presence of 0.02 percent NaCN in the ammonium carbonate is noted but is interpreted as a permissible contaminant because it is not mentioned in the claims and not discussed in the specification. The autoclave temperature is then raised to 300° C. and corresponding pressure of 650 p. s. i. for 2 hours. The excess ammonia and oxygen are presumably vented to a gasometer but are not mentioned, and the cooled solution is put through thickeners and filters, settling and filtering rapidly and with iron in a partly hydrated oxide form. Washing was done with ammonium carbonate solution and followed by water. The ore contained 0.25-1.5 percent Ni and tailing analysis of a test made under above conditions was 0.05 percent Ni and 0.03 percent Co.

The clarified ammonium carbonate solution was pumped into a second autoclave without ammonia or air and raised to 175 p. s. i. and 200° C. for 2 hours, with resulting precipitation of (presumably) mainly Ni carbonate (Co not mentioned). The filtration and return of ammonium carbonate to cycle are the final steps. The disposal of wash liquors is not mentioned but we must presume they are boiled off to the point of keeping a solution balance. Ni carbonate is not very stable, and some hydroxide might easily be assumed. The main ammonium carbonate solution thus circulates through two autoclaves and the leaching equipment. Ammonia is claimed to be used to keep Ni in solution in the leaching autoclave, and the form of the soluble Ni (or Co salt) is not discussed * * *. The process was designed for straight laterite and may leave no value on serpentine.

103. MINING JOURNAL (LONDON). Nickel-Cobalt Discovery in Cuba. Vol. 240, No. 6143, May 15, 1953, p. 576; Eng. Index, 1953, p. 703.

An ore body containing 40 million tons of Ni is in the Moa Bay area. The ore-treatment process involves the use of leaching with sulfuric acid. Annual production is estimated to be 30 million pounds of Ni, with 3 million pounds of Co to begin in 1955. Also included is a review of Ni sources throughout the world.

104. MIKONOV, A. A. [The Upper Ufalet Nickel Combine—Urals.] *Tsvetnye Metal*, 1932, pp. 246-251; Chem. Abs., vol. 27, 1933, p. 3424.

The ores occur mostly as claylike products of weathering of serpentines, limestones, shales, etc., with embedded silicate minerals of Ni. The resources

are estimated at 50,000 tons of Ni, about one-third of which is contained in rich ores (4 percent Ni), and the rest in poorer grade ores. Smelting and refining works were built to produce 3,000 tons of Ni yearly.

NONOXIDIZED ORES

105. ANAZAWA, KENJI (Furukawa Research Lab.). [Metallurgy of Nickel.] Jour. Electrochem. Soc., Japan, vol. 16, 1948, pp. 100-105; Chem. Abs., vol. 44, 1950, p. 9314e.

The industrial processes for the metallurgy of Ni used during the war are described: (a) Production of raw Ni from arsenide or Ni ores (10 percent); (b) from the byproducts of Pb and Zn metallurgy in Burma; (c) electrolytic separation of Ni and Co; (d) manufacture of extra-pure Ni; and (e) recovery of Ni from poor Japanese ores.

106. BRYCK, P. LEVANTO, K. I., MAKINAN, E., AND RYSELIN, J. Outokumpu's Copper Smelter Doubles Output During War. Eng. and Min. Jour., vol. 148, No. 1, January 1947, pp. 68-72; Eng. Index, 1947, p. 261.

Outokumpu, in Finland, is engaged in mining, milling, smelting, and refining Cu; it also produces pyrite-pyrrhotite concentrate. Also discussed are the history of the company; Outokumpu's mine and concentrator; the Nivala and Ylogjarvi mines; the Harjavalta Cu and Ni smelter; the Pori metal works.

107. DRYBROUGH, JOHN. A Nickel-Copper Deposit on Hudson Bay. Canadian Min. Met. Bull., vol. 227, 1931, pp. 390-402; vol. 236, 1931, pp. 1396-1399; Chem. Abs., vol. 26, 1932, p. 1547.

Exploration on Hudson Bay, 300 miles north of Fort Churchill, showed a Cu-Ni ore zone. The massive sulfide assayed Cu 1.28 percent, Ni 9.25 percent, and Pt 0.20 oz. per ton; the disseminated sulfide assayed Cu 1.19 percent, Ni 3.10 percent, and Pt 0.08 oz. Preliminary milling tests on low-grade ore (0.85 percent Cu and 1.75 percent Ni) gave recoveries of Cu 90, Ni 85, and Pt 90 percent.

108. GALLO, A. [Treatment of Pyrite-Roasting Residues.] Industrie chimique, vol. 28, 1941, p. 9, et seq.; Chem. Zentralb., vol. II, 1942, p. 88; Chem. Abs., vol. 37, 1943, p. 4339^a.

Suitable liquid extraction processes, the sulfate-roasting, chlorination-roasting, and so-called dead-roasting methods for obtaining Cu, Zn, Pb, Co, Ni, Ag, and Au from metallurgical residues are described. Their application for making the roasting residues suitable for raw materials for blast-furnace Fe is discussed. Iron oxide dyes and $\text{Fe}_2(\text{SO}_4)_3$ are also produced from the residues.

109. HOWAT, D. D. Nickel in Wartime Germany. Chem. Age, vol. 55, No. 1416, Aug. 17, 1946, pp. 191-194; Eng. Index, 1947, p. 753.

Discusses the recovery from Finnish low-grade Cu-Ni ores; production of Ni powder at plant of I. G. Farbenindustrie, A. G., at Oppau, Germany; volatilization treatment, smelting and refining; horizontal converters; treatment of Cu-Ni residues; manufacture of Fe powder; and control of particle size.

110. HUTTL, J. B. Howe Sound's Cobalt Mine Rapidly Nearing Production. Eng. and Min. Jour., vol. 151, No. 10, October 1950, pp. 89-91; Eng. Index, 1951, p. 225.

The Blackbird mine at Forney, Idaho, is now being equipped with a 600-ton mill and surface plant. The output will augment United States supply of this important metal, which is now largely obtained abroad and is needed for making special alloy steels.

111. ———. Idaho Cobalt for United States Defense. Eng. and Min. Jour., vol. 152, No. 12, December 1951,

pp. 78-80 and 121; vol. 151, No. 10, 1950, pp. 89-91; Eng. Index, 1952, p. 196.

A report of progress on the new mine and mill of the Calera Mining Co., is given. The Blackbird mine in central Idaho will produce 3 million pounds of Co annually, with a substantial tonnage of Cu. The Co product will be treated in a refinery being built near Garfield, Utah. The mining, ore treatment, and refining are reviewed, with the general aspect of the Co problem.

112. INTERNATIONAL NICKEL CO. The Operations and Plants of International Nickel Co. of Canada, Ltd. Canadian Min. Jour., vol. 67, 1946, pp. 311-554; Chem. Abs., vol. 40, 1946, p. 4632^a.

Information is included on milling, smelting, and refining of Cu, Ni, and Pt and uses of Ni.

113. INTERNATIONAL NICKEL CO. OF CANADA, LTD. Metallurgical Improvements in the Treatment of Copper-Nickel Ores. Trans. Canadian Inst. Min. and Met., vol. 51, pp. 356-357 (in Canadian Min. and Met. Bull. 434, 1948); Chem. Abs., vol. 42, 1948, p. 6286d.

In the last 10 years the Ni and Cu content of the flotation tailings has been cut in half. The use of preheated air in reverberatory furnaces has effected a fuel saving. In the Orford process the liquid converter matte is now poured at lower temperature, 1,400° F., into pots, making for better Ni-Cu separation and less thermal shock to the pots.

Improvements in mechanical operating details and plant maintenance are discussed.

114. KNICKERBOCKER, R. G. Smelting of Nickel-Copper Sulfide Ores. Conf. Met. Research, Met. Div., Bureau of Mines, Salt Lake City, May 1940, pp. 19-27; Chem. Abs., vol. 34, 1940, p. 4709^a.

Methods of recovering Ni, Cu, and precious metals from ores of the Bunkerville district in Nevada are given. Flowsheets for the Orford, Hybinette, and Bureau of Mines electrometallurgical pilot-plant methods for the separation of Cu and Ni and recent industrial applications of electric-furnace smelting to Ni-Cu and Cu ores are given, and the various processes are discussed (14 refs.).

115. LOMAS, J. Cobalt. Mine and Quarry Eng., vol. 17, No. 4, April 1951, pp. 128-130; Eng. Index, 1951, p. 224.

The origin and characteristics of Co are treated. The metal can be extracted from smaltite (CoAs_2), cobaltite ($\text{CoS}_2 \cdot \text{CoAs}_2$), linnaeite (Co_3S_4), erythrite ($\text{CoAs}_2 \cdot \text{O}_8 \cdot 8\text{H}_2\text{O}$), asbolite $\text{CoO}_2 \cdot \text{Mn}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and hercynite. The richest sources are in Belgian Congo. Discussed also are its use in pigments, in steel, and in tungsten carbide. Electroplating with Co is discussed.

116. LOW, BELA. A Nickel-Copper Deposit in New Brunswick, Canada. Eng. and Min. Jour., vol. 130, 1930, pp. 115-118; Chem. Abs., vol. 24, 1930, p. 4489^a.

Near St. Stephen in New Brunswick, a Ni-Cu prospect was opened 18 months ago. The geology of the area, exploration work, magnetic surveys, and metallurgical research are briefly outlined. Total recoveries of Ni and Cu in the sulfate leach, and Ni-flotation figured back to the Cu and Ni content of the roasted material show Ni recovery by leaching, 14.9 percent; Ni recovery in Ni concentrate, 58.4 percent; total Ni recovery, 73.3 percent; Cu recovery by leaching, 87.5 percent; Cu recovery in Ni concentrate, 8.9 percent; total Cu recovery, 96.4 percent. The metallurgical research indicates that the objective of recovering Ni, Cu, Fe, and S in separate marketable products can be accomplished. Tables show flotation tests and estimated marketable recoveries from 100 tons of ore.

117. MUTER, J. R. The Sherritt Gordon Lynn Lake Mining Project (Lynn Lake, Manitoba, Canada). Trans. Canadian Inst. Min. and Met., vol. 58 (in

Canadian Min. and Met. Bull., vol. 519, 1955, pp. 385-389; Chem. Abs., vol. 49, 1955, p. 13043b.

Milling, by Drake, R. T., work cited above, pp. 390-395. The chalcopryite and pentlandite float readily, and 90 percent of the Cu as chalcopryite and 55 percent of the Ni as pentlandite float in the first 5 minutes of flotation time. Compositions of mill products and screen products are given.

Refining at Fort Saskatchewan, by Nashner, Sydney. The Ni refinery started complete operations in August 1954 and reached rated capacity early in 1955. The refinery was designed and constructed on the basis of treating Lynn Lake concentrate analyzing approximately Ni 12, Cu 1.5, Co 0.7, Fe 30, S 28, and inerts 28.1 percent. A metals-plant flowsheet and plant layout are given.

118. NORDIN, W. Petsamo Nickel. Metal Ind., vol. 73, No. 10, Sept. 3, 1948, pp. 183-185; Eng. Index, 1948, p. 832.

Introduction is written by A. G. Robiette. The article presents an account of the development of the Ni deposits in the district of Finland before World War II, including descriptions of smelting plants, electric furnaces, mining equipment, and operating data.

119. RICE, H. R. Annual Review of Technical Advances in Canada's Mineral Industries. Part 2. In Milling and Process Metallurgy. Canadian Min. Jour., vol. 75, No. 2, February 1954, pp. 119-120; Eng. Index, 1954, p. 757.

Reviews Canadian metallurgical developments and trends in 1953. Subjects covered are crushing and grinding, concentration with cyclones, use of heat in flotation, and extractive metallurgy of Ni, Cu, and Co ore.

120. ROBY, R. N. Investigation of Copper-Nickel Deposits of Stillwater Complex, Stillwater and Sweetgrass Counties, Mont. Bureau of Mines. Rept. of Investigations 4431, 1949, 10 pp.

Cu-Ni sulfides occur in pods and lenses in norite and hornfels at base or south side of zone of layered basic igneous rocks known as Stillwater igneous complex. This zone is 1 to 5 miles wide and about 30 miles long in a general east-west direction. Diamond-drill data and core and sludge analyses are reported. A concentration test was run on a large composite sample.

121. SCHÖN, Edv. [Working Up Valuable Constituents Other Than Copper and Iron by the Treatment of Copper-Containing Pyrites Cinders According to the Extraction Method.] Tek. Tidsskr. Uppl. C. Kemi., vol. 62, 1932, pp. 89-91; Chem. Abs., vol. 27, 1933, p. 931.

Discusses methods proposed for working up Cu, Zn, Co, Ag, and Na₂SO₄ present in the liquors obtained on leaching chloridized roasted pyrites cinders.

122. STØREN, R. [Veins of Cobalt, Nickel, and Native Silver in Kongsberg District, Norway.] Tidsskr. Kjem. og Bergvesen, vol. 11, 1931, pp. 95-97 (see Chem. Abs., vol. 25, 1931, p. 3935); Chem. Abs., vol. 26, 1932, p. 3758.

Chemical analyses and microscopic examinations show that some of the Ag veins in the Kongsberg district carry small quantities of cobalt-nickel arsenides as a thin coating on the surface of the Ag. Støren discusses the mechanism of formation of this coating, points to the analogy of the Ag mines at Temiskaming, Canada, and gives a survey of practical experience of smelting such ore.

123. THOMPSON, J. F. [Nickel Progress During the Last Decade.] Rev. mét., vol. 32, 1935, pp. 509-517; Chem. Abs., vol. 30, 1936, p. 1709⁴.

A survey of recent advances. At the Frood mine in the Sudbury district, the ore after grinding is floated,

eliminating the gangue and separating Cu-rich and Ni-rich portions. The Ni-rich portion is roasted in Herreshoff furnaces above reverberatories into which hot calcines are fed. The matte from the reverberatories, assaying 25 percent Ni, is blown in Pierce-Smith converters to a composition of Cu 42 percent, Ni 37 percent, and S 20 percent, while the slag is returned to the reverberatories. The "tops-and-bottoms process" depends solely on the solubility of CuS in Na₂S, which is obtained by roasting Na₂SO₄, C, and matte. The CuS fraction, floating on top, is removed after cooling. The "bottoms," containing the Ni, are crushed, washed, and sintered and melted with C into anodes, which are placed in cloth bags and electrolyzed after electrolyte purification. In another procedure the crushed and reduced "bottoms" are treated by the Mond process.

124. TIMM, W. B., AND OTHERS. Ore Dressing and Metallurgy, January to June, 1934. Canadian Dept. Mines, Mines Branch Rept. 747, 1935, 209 pp. (see Chem. Abs., vol. 29, 1935, p. 6861⁵); Chem. Abs., vol. 29, 1935, p. 7238⁷.

Gives results of concentrating and extraction tests on Ni-Cu ores and five other types of ore.

125. WARREN, H. V., AND THOMPSON, R. M. Mineralogy of Two Cobalt Occurrences in British Columbia. Inst. Min. and Met. Bull. 470, 471, January 1945, 18 pp.; Eng. Index, 1945, p. 232. Author's reply to discussion of paper in Inst. of Min. and Met. Bull. 479, July 1946; pp. 33-35. This is also indexed in British Abs., vol. A-1, 1945, p. 104. See also Trans. Inst. Min. and Met., vol. 54, 1944-1945, pp. 201-230, indexed in British Abs., 1948, vol. A-1, p. 41. and Western Miner, vol. 18, No. 5, May 1945, pp. 34-41.

At the Nickel Plate Mountain mine at Hedley, Co in the ores is carried by cobaltite, and by löllingite-safflorite at Little Gem prospect in Lillooet Mining Division. This has been established by identification in polished sections of Co minerals. The economic possibilities of producing Co and other Co prospects are reviewed. The appendix contains an article by F. A. Forwood and A. G. Lyle on the recovery of Co, Cu, and Au from arsenical concentrates by roasting and leaching.

INTEGRATED SEQUENCES OF OPERATIONS NONSPECIFIED ORES

126. BOGITCH, B. [Nickel Industry in the Urals.] Rev. mét., vol. 36, 1939, pp. 421-428 (see Chem. Abs., vol. 34, 1940, p. 349¹); Chem. Abs., vol. 34, 1940, p. 1951¹.

Three main deposits of Ni ores are known—Khalilov, Akermanovka, and Actuba—all having a Ni content of about 2 percent, with the total content of the metal estimated at several hundred thousand tons. Only open-pit mining is used, and the ores are smelted without dressing. Only 1 modern plant at Orsk is in operation; 2 others melting the ore are old and obsolete. The ore is sintered, fluxed to take care of excessive gangue content, and melted for matte in 1.60- by 13.4-m. water-jacketed furnaces. Low Ni content is taken care of by slow descent of the charge and prevention of fine accumulation in the center of the furnaces. About 0.25 percent Ni is lost in the slag and 350 kg. per ton of coke used, producing matte with 30 percent Ni, 20 percent S, and 50 percent Fe. It is purified in 5- to 10-ton magnesite-lined converters.

127. CARRERAS, R. S. [Cobalt From Minerals.] Swiss Patent 145,490, July 10, 1929; Chem. Abs., vol. 26, 1932, p. 37.

Co is extracted from minerals containing Co, Cu, and alkaline-earth metals by submitting the mineral

to the action of H_2SO_4 and NaCl , electrolyzing the solution so obtained to eliminate the Cu , concentrating the resulting solution, and cooling to precipitate the alkaline earth metals, and finally cooling and concentrating the resulting liquor to separate crystals of CoSO_4 . The Co is then obtained by electrolysis of the CoSO_4 solution.

128. CARRERAS, R. S. Cobalt From Complex Ores. U. S. Patent 1,928,340, Sept. 26, 1933; Chem. Abs., vol. 27, 1933, p. 5655.

Ores such as those containing Co , together with Cu and alkaline-earth gangue, are subjected to the action of H_2SO_4 and NaCl to attack the metals of the ore. The solution thus obtained is electrolyzed by using unattackable anodes, such as graphite, and thin-sheet Cu cathodes until all the Cu has been eliminated. The electrolyte is then concentrated by evaporation to favor precipitation of alkaline-earth salts, the liquid is filtered, concentrated further, and cooled in order that the content of Co may separate as cobalt sulfate crystals. The separated cobalt sulfate is then dissolved, and the solution so formed is electrolyzed to obtain metallic Co .

129. DE LEZANA Y ARANA, ANTONIO. [Chemical Method to Obtain Pure Copper, Nickel, and Cobalt From Minerals, Scraps, and Alloys.] Spanish Patent 215,519, May 24, 1954; Chem. Abs., vol. 49, 1955, p. 9477b.

The raw materials (minerals or concentrates) are roasted and lixiviated with sulfates. The solutions are treated with ammonia to precipitate the metal as a hydroxide. More ammonia is added to redissolve the hydroxides. After filtration, the filtrate is heated in an autoclave at 235°C , which causes dissociation and precipitation of the Cu . The Ni and Co are separated in a similar manner.

130. GARDNER, DANIEL (assigned to Virginia Metal Industries Inc.). Recovery of Chromium and Related Metals From Iron Ores. U. S. Patent 2,409,428, Oct. 15, 1946 (see Chem. Abs., vol. 38, 1944, p. 5790¹); Chem. Abs., vol. 41, 1947, p. 4765a.

A finely ground mixture of raw ore, coke, and $\text{Ca}(\text{OH})_2$ is heated in a kiln to convert the metal oxides to Fe_2O_3 , Cr_2O_3 , Mn_2O_3 , CoO , and NiO . An alkaline-earth hydroxide should be present in excess to react with all of the silica and alumina. After quenching in a lime solution, the gangue is separated by flotation and removed. A second heating with $\text{Ca}(\text{OH})_2$, steam, and air at $500^\circ\text{--}800^\circ\text{C}$ converts the Cr and Mn to calcium chromate and calcium permanganate, which, when dissolved in water containing glycerol, are separated from the insoluble material. The Ni may then be leached out from the insolubles with $\text{NH}_4\text{OH}\text{--}\text{NH}_4\text{Cl}$ solution, and precipitated with sodium hydroxide. An alternative process omitting the first kiln treatment is detailed.

131. KISSOCK, ALAN. Treatment of Nickel Ores Containing Iron. U. S. Patent 2,341,873, Feb. 15, 1944; Chem. Abs., vol. 38, 1944, p. 4243⁹.

A process is employed for separating Ni , with Co and Cu when also present, from ores containing a relatively high percentage of Fe , which involves reduction of the oxides of Ni , Co , and Cu , but not the oxide of Fe , as by C or a hydrocarbon, and subjecting the reduced ore to treatment with an aqueous HOCl solution as solvent for the reduced metal.

132. MUKOYAMA, MIKIO (assigned to the Minister of Commerce and Industry). [Extraction of Nickel and Cobalt From Ore.] Japanese Patent 176,809, Oct. 15, 1948; Chem. Abs., vol. 45, 1951, p. 4197g.

The ore, containing Ni , Co , or Fe as oxide, sulfide, or arsenate, is heated at $400^\circ\text{--}800^\circ\text{C}$ in air, then heated at $300^\circ\text{--}600^\circ\text{C}$, with reducing gases, to make a solid solution of Ni and Co and an iron salt or Fe_2O_3 ,

and finally oxidized by heating to a point below 300°C . A magnet is used for separating out the solid solution of Ni and Co . Ni and Co are extracted from the solid solution of Ni and Co with a dilute mineral acid in an autoclave at a temperature below 300°C in the presence of O_2 .

133. SCHWELLNUS, C. M. The Nickel-Copper Occurrence in the Bushveld Igneous Complex West of Pilandsbergen. Union of South Africa, Dept. Mines, Geol. Series Bull. 5, 1935, 36 pp.; Chem. Abs., vol. 30, 1936, p. 57⁴.

The source, grade, treatment, and uses of these ores are discussed.

134. WHITTMAN, J. [Electrometallurgical Production of Cobalt and Copper in the Belgian Congo.] Jour. du four élec., vol. 56, 1947, pp. 55-56; Chem. Abs., vol. 44, 1950, p. 6741e.

The Co concentrates, scoria, and dross are fed into an electric arc furnace, and CaO and coke are added. A white alloy containing Fe , Cu , Si , and 42 percent Co is produced, and this is granulated in H_2O . The heavy Cu granules are cast into red ingots containing only a trace of Co , and these are refined in a rotating furnace. The scoria, containing 17 percent Co , is returned to the arc furnace. The electrolytic refining of Co involves a series of operations to eliminate Fe and Cu . The salts of Co are selectively precipitated by addition of CaO , and the hydrated precipitated Co oxide is redissolved in dilute acid. The Co is then deposited on Fe plates, from which it is readily stripped, fed into a three-phase Lectromelt furnace, refined, cast, and granulated.

OXIDIZED ORES

135. BARAGWANATH, J. G., AND CHATELAIN, J. B. Development and Equipment of the Nicaro Nickel Project. Min. and Met., vol. 26, 1945, pp. 391-394; Chem. Abs., vol. 40, 1946, p. 4990¹.

The ore body is a lateritic deposit altered from the underlying serpentinized peridotite by the action of the weather in leaching out silica and magnesia. Nickel remained and was concentrated apparently as a colloid of uncertain composition distributed irregularly through the ore body. Treatment of the ore is described in detail. It is crushed, dried, ground and partly reduced, leached with an ammoniacal ammonium carbonate solution, and precipitated as a basic carbonate by distillation and recycling of ammonia. The carbonate is ignited to nickelous oxide, which is marketed. Apparatus and a flowsheet are described.

136. BOGATSKII, D. P. [New Complex Methods of Chemical Treatment of Oxidized Nickel-Cobalt Ores With Utilization of Waste Sulfur Dioxide.] Bull. Acad. Sci., U. R. S. S., classe sci. chim., 1944, pp. 272-282 (English summary); Chem. Abs., vol. 40, 1946, p. 3375⁹.

The conditions of reduction and chemical treatment of various silicate oxidized Ni ores were studied. It was shown that direct reduction and leaching of the reduced ores by weak H_2SO_4 give the most satisfactory results even under unfavorable conditions. The process gave up to 94-99 percent extraction of Ni from low-grade and waste silicate-oxidized Ni ores. The process of leaching requires but 15-30 minutes, with 60- to 80-ton expenditure of H_2SO_4 for 1 ton of Ni being reduced to but 30-40 tons in comparison with other methods. The preliminary reduction of the ore is necessary for efficient utilization of H_2SO_4 , with the optimum results being obtained at $98^\circ\text{--}100^\circ\text{C}$ with 5 percent H_2SO_4 being used on ore that was reduced 2 hours at 800°C . Some advantages appear in a preliminary

extraction with 3 percent H_2SO_4 in the cold. A considerable saving of the acid is effected by regeneration.

137. CARON, M. H. [Working Up Oxidized Nickel Ores of Low Nickel Content.] *De Ing.*, vol. 54, No. 2, pp. 15-27; *Neues Jahrbuch Mineral., Geol., Ref.* II, 1939, p. 750; *Chem. Abs.*, vol. 34, 1940, p. 2299¹.

After a brief account of methods dealing with such ores, Caron describes his own, which depends on the selective reduction of the free or combined NiO in the ore with selective extraction of reduced Ni in the ore, whereby the liquor, an ammoniacal ammonium carbonate, is completely recovered by distillation, precipitating basic nickel carbonate, which is calcined to NiO ; this leaves only a small amount of ammonia in the residue.

138. ———. [Extracting Nickel and Cobalt From Ores.] *Netherlands Patent* 62,693, Mar. 15, 1949; *Chem. Abs.*, vol. 43, 1949, p. 4998g.

Ni and Co ores have been prepared for extraction with a solution of ammonium salts effected by hot reduction followed by cooling under exclusion of O . Addition of a halide was useful in lowering the temperature of reduction and in increasing the extraction. Addition of small quantities of S , as pyrite (As , Te , Se), in addition to the halide (NaCl), increased extraction. For example, serpentized peridotite with 2.12 percent Ni gave, without any addition, 56 percent of its Ni . Addition of 0.375 percent NaCl increased it to 66 percent and the NaCl plus 3 percent pyrite to 86 percent.

139. ———. (Delft Univ., Delft, Netherlands). *Fundamental and Practical Factors in the Ammonia Leaching of Nickel and Cobalt Ores.* *Jour. Metals*, vol. 188, No. 1, 1950; *Trans. AIME*, pp. 67-90; *Metals Rev.*, vol. 23, 1950, No. 2, p. 20 (6B); *Chem. Abs.*, vol. 44, 1950, p. 1862f.

Brief statements are given of investigations of various fundamental and practical factors in the ammonia-leaching process for Ni and Co ores. The process was in large-scale operation at Nicaro, Cuba, as an emergency war measure in World War II. Descriptions of this plant and its operations have been published, but these descriptions mainly covered installations and plant-scale results; the present article gives a considerable amount of hitherto unpublished data on various phases of the process, including conditions for ore reduction, leaching, distillation and other details. Possibilities as to further development and results of tests on ores other than the Cuban laterites are also included.

140. ———. Some Aspects in Connection With the Application of the Ammonia Leaching Process. *Ingenieur*, vol. 66, No. 32, Aug. 6, 1954, p. M25-9 (in English); *Eng. Index*, 1954, p. 758.

Discussed are: Requirements for commercial application of process, passivity and activation, simultaneous dissolution of Ni and Co as observed under batch test conditions, concurrent vs. countercurrent leaching, agitator capacities as needed for process requirements, choice of metals for leaching equipment.

141. DEAN, R. S. Cobalt. *Bureau of Mines Rept. of Investigations* 3600, 1941, pp. 42-44; *Chem. Abs.*, vol. 36, 1942, p. 4068⁵.

"The cobalt mineral prevalent in the district has been identified as stainerite, $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The stainerite is associated with malachite, cuprite, and chrysocola in dolomite, calcite, goethite, and quartz gangue. The Ore-Dressing Section of the Metallurgical Division investigated beneficiation methods and advocated a bulk flotation procedure for recovering stainerite. The copper minerals floated with the stainerite to a considerable extent. Differential flotation tests for separation of cobalt and copper indicated that concentrates of

cobalt could not be prepared sufficiently free of copper to meet specifications for cobalt oxide, except at great expense to recovery.

"Leaching of bulk concentrates, purification of solutions, and electrolytic deposition of high-purity cobalt metal presented a more favorable recovery method, and small-scale laboratory work was inaugurated to establish optimum conditions before substantiation by pilot-scale operation.

"The run-of-mine cobalt ore averaged approximately 1 percent cobalt oxide and 0.5 percent copper and obviously required concentration before leaching. The flotation involved sulfidization with sodium, barium, or ammonium sulfide, followed by xanthate collector, pine-oil frother, and sodium silicate depressant. Fine grinding (approximately 200-mesh) was necessary to liberate minerals. The concentrates averaged 14-15 percent Co_2O_3 and 12 percent copper, with minor amounts of iron, zinc, arsenic, manganese, nickel, and lead. The dissolution treatment involved mechanical agitation of the concentrates pulped with water while sulfur dioxide gas was introduced in a slow bubbling stream for 15 to 24 hours. Approximately 98-percent extractions were consistently attained." Removal of copper, iron, arsenic, and other impurities resulted in a solution in which cobalt carbonate could be isolated by careful pH control. "For electrolytic deposition of cobalt, the precipitated cobalt carbonate was redissolved in sulfuric acid (spent anolyte from the electrolytic cell). The electrolyte found most satisfactory contained 50-100 gm. CoSO_4 , 50 gm. boric acid, and 5 gm. sodium fluoride per liter * * *."

142. DUFOUR, M. F., AND HILLS, R. C. (assigned to Nicaro Nickel Co., Nicaro, Cuba). *Nickel From Cuba—Nicaró Produces Nickel Oxide by Leaching With Ammonia.* *Chem. Industries*, New York, vol. 57, 1945, pp. 621-627; *Chem. Abs.*, vol. 41, 1947, p. 2671e.

Describes design, equipment, and operation of a plant using the Nicaro process for recovering nickel oxide from Cuban lateritic ore. The ore is reduced and leached with a mixture of NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ in the presence of O_2 to form soluble NH_3 complexes. Basic nickel carbonate is precipitated from this solution by stripping the NH_3 with steam, and the precipitate is calcined to NiO . The NH_3 is recovered.

143. ECHO DES MINES ET DE LA MÉTALLURGIE. *Les Mines et la fonderie de nickel de la Société "Le Nickel" en Nouvelle Calédonie.* [Nickel Mines and Foundry of "Le Nickel" Co. in New Caledonia.] Nos. 3464, 3466, and 3467, January 1954, pp. 37-41; March, pp. 171-175; and April, pp. 245-246; *Eng. Index*, 1954, p. 713.

The Ni mines and foundry of "Le Nickel" Co. in New Caledonia, mining operations, ore handling, and ore conveying to the port terminal are discussed. The features of the Ni foundry at Domiambo are related.

144. *ENGINEERING AND MINING JOURNAL.* *Nicaró Resumes Production.* Vol. 153, No. 3, Mar. 1952, pp. 88-90; *Eng. Index*, 1952, p. 675.

Full production of Ni plant in Oriente Province, Cuba, is scheduled for June 1, 1952, at an annual rate of 15,000 tons of nickel. In the process, lateritic nickel iron ore is converted to the refined oxide. The ore body comprises ore zones represented by serpentine and limonite, which lie over the altered serpentine. The processes of reduction roasting, cooling, leaching, and precipitation are described.

145. *GENERAL SERVICES ADMINISTRATION. RESEARCH LABORATORY OF THE NICARÓ NICKEL PROJECT. Progress and Research on Problems Encountered in the Plant Operation. Monthly Reports, 1952-53.* Available from General Services Administration, Washington, D. C.

Virtually all key operations in the operating plant of the Nicaro Nickel Project were investigated by the research laboratory. Among topics investigated were separation of Ni and Co; reduction of serpentine; Ni recovery from laterite influenced by temperature; reduction in rotary kilns as against that in Herreshoff furnaces; uses of stronger ammonia leach; reoxidation (after reduction to metal); influence of asphalt residues on ammonia leaching; effect of moisture additions to the ore. The treatment most favorable for Ni recovery from serpentines differs from that of laterites. Should they be treated separately? Many other investigations of operational phases are reported.

146. GROTHE, J. D. (assigned to The Dorr Co.). Treating Lateritic Ores. U. S. Patent 2,363,315, Nov. 21, 1944; Chem. Abs., vol. 39, 1945, p. 3237².

Ores containing Ni, Cr, and Fe, mainly in the form of limonite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), are ground and roasted to convert the limonite to the heavier magnetite (Fe_3O_4). The reducing-roast conditions are such that the nickel silicates are reduced to Ni and the limonite changes to magnetite. This is insured by maintaining a reducing roast at 900° C. or higher. The roasted ore is aerated while being leached with an ammoniacal solution of $(\text{NH}_4)_2\text{CO}_3$. A $[\text{Ni}(\text{NH}_4)_2\text{CO}_3]$ complex is leached out and subsequently decomposed with steam to yield NiCO_3 . From the remaining thickened and filtered pulp chromite (FeCr_2O_4) is removed by flotation, leaving a purified Fe ore. This process enables the 0.5–1.5 percent of Ni commonly present in such ores to be recovered in a marketable form and also permits recovery of the 1.5–4.0 percent Cr present. A flowsheet is given.

147. HAMASUMI, MATSUIRO, ISAWA, MASANOBU, SUZUKI, RENSACKU, KAMEDA, MITSUO, AND HOSODA, KAORU (Tōhoku Imp. Univ., Sendai, Japan). [Commercial Extraction of Cobalt From Asbolite Ore of Kimmō Island.] Bull. Research Inst. Mineral Dressing Metal., vol. 1, 1942, pp. 3–50; Chem. Abs., vol. 45, 1951, p. 881.

The asbolite ore (a conglomerate of psilomelane and silica, Co 0.3 percent) was crushed, concentrated by gravity, roasted at 550°–700° C., and then leached with 5 percent H_2SO_4 at 80° C. Repeated countercurrent leaching increased the yield. From the solution, Cu was removed by cementing with Fe scrap and by adding Na₂S to the filtrate after adjusting to pH 3.5–5.0 with NaOH. Co was precipitated as CoS . This was roasted at 850° C. in air to CoO and then reduced with H₂ at 1,100° C. to Co. The metallic Co thus obtained contained Co 83.66, Ni 10.83, Fe 3.32, Cu 0.03, Mn 0.04, and insoluble matter 1.93 percent.

148. HEDLEY, N., AND KRESS, J. J. (assigned to American Cyanamid Co.). Treatment of Garnierite Ores. U. S. Patent 2,349,223, May 16, 1944; British Abs., 1947, p. B-1-220.

Ore containing nickel and iron silicates is mixed with C and subjected to a reducing roast at 800°–1,000° C., preferably 900° C., under conditions which reduce the NiO to Ni. The mass is leached with an aqueous solution of SO_2 , and insoluble material is separated. The liquor is boiled to precipitate part of the Ni as NiS , and the remainder is precipitated with an amount of Na₂S insufficient to precipitate any Fe.

149. HILLS, R. C., AND DUFOUR, M. F. (assigned to Nicaro Nickel Co.). Removal of Sulfur During the Recovery of Nickel From Ores. U. S. Patent 2,408,311, Sept. 24, 1946; Chem. Abs., vol. 41 1947, p. 4765b; British Abs., 1950, p. B-1-1079.

Nickel carbonate substantially free of sulfide may be precipitated from $(\text{NH}_4)_2\text{CO}_3$ leach solutions obtained by leaching reduced nickeliferous ores, by adding Na₂CO₃ before precipitating. The amount of

Na₂CO₃ added is 5–10 percent by weight of the sulfide content. If the sulfide is so high that some is left in the precipitate, the latter may be washed with Na₂CO₃. The temperature should be 150°–180° F.

150. HUNDHAUSEN, R. J., McWILLIAMS, J. R., AND BANNING, L. H. Preliminary Investigation of Red Flats Nickel Deposit, Curry County, Oreg. Bureau of Mines Rept. of Investigations 5072, 1954, 19 pp. 1954, 19 pp.

The geologic setting, distribution, and chemical and mineralogical composition of nickeliferous laterites and serpentines are reported. Also discussed are drilling and sampling methods, equipment and facilities for smelting research. A selective smelting procedure is found applicable to the ore.

151. INTERNATIONAL NICKEL CO. OF CANADA, LTD. Recovery of Nickel From Nickel-Containing Ores. British Patent 646,488, Nov. 22, 1950; Chem. Abs., vol. 45, 1951, p. 3788e.

This method of economically recovering Ni from lateritic ores containing small amounts of Ni is an improvement on the NH_3 process developed by Caron (Chem. Abs., vol. 44, 1950, p. 1862f). Here the ores are first reduced at a temperature above 650° C. (760°–870° C.), preferably in a reducing atmosphere, then oxidized at a temperature below 760° C., and reduced at 315°–550° C. The reducing atmosphere should contain a ratio of combustible gases to water vapor plus CO_2 of more than 50:50 by volume. The substantial amount of Fe reduced with the Ni at first is largely removed during the subsequent oxidation and rereduction. Continuing the process, the ore is next cooled to about 200° C. and then immersed in an ammoniacal leaching solution in which the Ni dissolves but the bulk of the ore remains insoluble. The Ni-containing ammoniacal solution is then treated in the usual manner to obtain a commercial Ni product.

152. KRUTOV, G. A., MAMEDOV, M. A., AND UL'YANOV, D. G. [Rare and Nonferrous Metals; Cobalt-Bearing Ores of the South Ural.] Trans. All-Union Sci. Research Inst. Econ. Mineral., U. S. S. R., vol. 147, 1939, pp. 5–19; Chem. Abs., vol. 34, 1940, p. 2742¹.

Reviews results of a survey of Co-bearing Ni and Mn deposits in the region, carried out by the Institute in 1934–37, and discusses tentative methods for recovering Co by complex treatments of the ores from technical and economic viewpoints.

153. LUTJEN, G. P. Nicaro Proves Lateritic Nickel Can Be Produced Commercially. Eng. and Min. Jour., vol. 155, No. 6, 1954, pp. 81–89; Chem. Abs., vol. 48, 1954, p. 12002c; Eng. Index, 1954, p. 713.

An altered serpentine on top of the hills at Nicaro, Cuba, contains up to 2 percent Ni. The mine supplies 4,000 tons of ore per day, averaging about 38 percent Fe and 1.37 percent Ni. At a –200-mesh grind, nickel minerals are reduced to metal and iron minerals to Fe_2O_3 by producer gas in 16-hearth Herreshoff furnaces at carefully controlled temperatures (593°–693° C.). Reduced ore is cooled to 175° C., quenched in NH_4OH , $(\text{NH}_4)_2\text{CO}_3$ liquor (11 percent NH_3), and aerated to oxidize and dissolve Ni. When the NH_3 is distilled (and recovered), a basic carbonate of Ni is precipitated, which is then calcined to NiO at about 980° C., sintered, and marketed.

154. McMILLAN, W. D., AND DAVIS, H. W. Nickel-Cobalt Resources of Cuba. Bureau of Mines Rept. of Investigations 5099, 1955, 86 pp.

The nickeliferous Fe ores of Cuba are the largest potential sources of Ni in the world. Reserves carrying 1 percent or more Ni are estimated at 356 million dry short tons, and those containing less than 1 percent are about 1,500 million tons. The production and reserves of Ni and Co of the world are briefly re-

viewed. The flowsheets of the operation at Nicaro are given, with a brief survey of the partial reduction, ammonia-ammonium carbonate recovery process. Over 3,700 dry tons of ore per day is dried, crushed, and reduced in Herreshoff furnaces with oil and producer gas. After being leached with ammonia-ammonium carbonate solution employing agitation and aeration, the solution is distilled off, leaving a nickel basic carbonate. This is calcined to NiO and so marketed.

155. MEYER, R. F. (assigned to Meyer Mineral Separation Co.). Treating Iron Ores. British Patent 377,705, Oct. 8, 1930 (*see Chem. Abs.*, vol. 26, 1932, p. 5539); *Chem. Abs.*, vol. 27, 1933, p. 3183.

In removing Cu, Co, and Ni from Fe ores the finely divided oxidized or roasted ore containing FeO or FeO·Fe₂O₃ is treated in a "quasiwet" condition maintained at least until the FeO has reacted with the gas employed. The temperature is then raised to decompose the ferrous salt formed and in the presence of air to form chlorides or sulfates of the metals to be removed, which are recovered by leaching. The ore may be preliminarily reduced to provide FeO therein.

156. MINING JOURNAL (LONDON). Treatment of Cuban Nickel Ores. Vol. 244, May 13, 1955, pp. 530 and 532; *Metals Rev.*, vol. 28, July 1955, No. 7, p. 31, item 110-B.

Discussed are: High economy of recovery, treatment of nickeliferous ores, and metallurgical investigations.

157. MIRONOV, A. A. [Production of Metal From Ufaley Nickel Ores.] *Tsvetnye Metal*, 1930, pp. 48-67; *Chem. Abs.*, vol. 27, 1933, p. 482.

"Ufaley Ni ore, containing SiO₂ 47.74, Al₂O₃ 12.74, Fe₂O₃ 18.34, CaO 1.12, MgO 4.03, Ni 4.36 percent, and no S, was smelted in a semicommercial plant. The ore was ground, mixed with gypsum and anthracite fines, and made into briquets containing 3.09-3.76 percent Ni. The briquets were smelted with coke in a small shaft furnace and then refined in small acid Bessemer converters. The product from the converters was ground to 60- to 100-mesh and heated in an oil reverberatory furnace at 1,100°-1,150° C. At this stage the S was reduced to 0.16-0.04 percent. The metal was ground again to 100-mesh and heated in the same furnace at 1,200°-1,250° C. for 10-12 hours until the S decreased to 0.01-0.02 percent. The NiO thus obtained was ground, mixed with rye flour, made into briquets, and heated in oil-fired furnaces at 1,200°-1,300° C. for 8-10 hours." The end product was metallic nickel containing Ni 98.9-98.0, Fe 1.5-1.9, S 0.01-0.08, Al₂O₃ 0.03-1.45, Cu 0.15, and Co 0.10-0.13 percent.

158. PAWEL, G. W. Possible New Sources of Nickel. *Min. and Met. (AIME)*, vol. 24, 1943, pp. 277-278; *Chem. Abs.*, vol. 37, 1943, p. 6610°.

The Caron-Clevenger ammonium carbonate leach can be used on low-grade ores, including garnierite.

159. PEDLIK, MIROSLAV. [Treatment of Low-Grade Siliceous Nickel Ores.] *Hutnicke Listy*, vol. 7, 1952, pp. 639-641; *Chem. Abs.*, vol. 49, 1955, No. 2, p. 803g, h, i.

Two methods tested in pilot plants are discussed; the first leads to ferronickel alloy I containing 6-10 percent Ni, and the second leads to a pure Ni containing Ni 99.9, Co 0.12, and S 0.001 percent. The yield of the latter method is 75 percent. I contains impurities like S 0.4-1.5 and P 0.1-0.6 percent and hence requires expensive refining. Average composition of the ore is: Ni 0.5-1.7, Fe 6-20, SiO₂ 40-60, MgO 7-16, CaO 1-3, and Al₂O₃ 2-8 percent. I is made by smelting the ore with coke (30 percent) in a rotary kiln at 1,200°-1,300° F., then cooled, ground in ball mills, and concentrated magnetically. The second method requires drying to 2 percent H₂O, fine grinding so that only 5 percent of particles is more than 0.15 mm., and reduction at 500° C. The latter is carried out within 3 hours in a Herre-

shoff kiln with gas obtained by partial combustion of coke with air and introduced into the kiln at 750°-800° F. By careful control of the reduction, Fe is not reduced to metal but to Fe₂O₃. The reduced ore is cooled to 100° F. in a reducing atmosphere so that reoxidation of Ni is prevented. The ore is then leached in an ammoniacal solution of (NH₄)₂CO₃ while air is introduced with vigorous agitation. The following reactions take place: $2\text{Ni} + \text{O}_2 + 2(\text{NH}_4)_2\text{CO}_3 + n\text{NH}_4\text{OH} = 2\text{Ni}(\text{NH}_3)_6\text{CO}_3 + n\text{H}_2\text{O}$; $2\text{Fe} + 2(\text{NH}_4)_2\text{CO}_3 + n\text{NH}_4\text{OH} = 2\text{Fe}(\text{NH}_3)_6\text{CO}_3 + n\text{H}_2\text{O}$; $\text{Fe}(\text{NH}_3)_6\text{CO}_3 + n\text{O}_2 + n\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + (\text{NH}_3)_6\text{CO}_3 + n\text{NH}_4\text{OH}$. The filtrate is distilled with steam to precipitate Ni according to the following reactions: $2\text{Ni}(\text{NH}_3)_6\text{CO}_3 + \text{H}_2\text{O} = \text{Ni}(\text{OH})_2 \cdot \text{NiCO}_3(\text{II}) + 8\text{NH}_3 + \text{CO}_2$. The suspension is filtered on a rotary vacuum filter and produces a cake having the following composition: Ni 45-52, Fe 0.2-0.5, SiO₂ 4-6, and Mn 2-3. NH₃ and CO₂ are absorbed in H₂O. II is dissolved in H₂SO₄, and the solution containing 80-90 g./l. of Ni is electrolyzed at 60°-70° C., pH 4-5, 4 amp./sq. dm. and 3 v.

160. REITLER, E. [Nickel From New Caledonia Nickel Ores.] *Metallbörse*, vol. 24, 1934, pp. 1530-1531 and 1562-1563; *Chem. Abs.*, vol. 29, 1935, p. 2121°.

Describes the occurrence and extraction of Ni ores.

161. SHELTON, F. K. Metallurgical Treatment of Cobalt Ores From the Goodsprings Mining District, Nev. Bureau of Mines Rept. of Investigations 3836, 1946, 34 pp.; *Chem. Abs.*, vol. 40, 1946, p. 5677°.

Stainierite (Co₂O₃·H₂O) is amenable to concentration commercially by flotation of hot pulps of finely ground ore. From an ore containing 0.5-1.0 percent Co, concentrates assaying 10-20 percent were produced. Tabling followed by flotation of the middling and tailing on high-grade ores was successful. Stainierite concentrate can be leached with combinations of H₂SO₄ and H₂SO₃ in aqueous solutions. SO₂ is a good solvent when used alone. Impure Co solutions are purified by cementation of Cu on Fe, Cu is precipitated as sulfide, and oxidation of Fe is usually by aeration and precipitation of oxidized Fe with pulverized calcite. Relatively high grade hydrated cobalt carbonate precipitates from the properly purified solution by treatment with aqueous solutions of soda ash within certain narrow pH ranges. Electrolytic Co deposits satisfactorily from an electrolyte containing 50 gm. per l. of cobalt sulfate, 50 gm. per l. of boric acid, and 5 gm. per l. of NaF. A current density of 25 amp. per sq. ft. and an electrolyte pH of 1.8-2.0 are recommended. Precipitated CoCO₃ is used to neutralize the spent electrolyte. An alternate method of producing electrolytic Co involves the use of 50 gm. per l. of cobalt sulfate and 50 gm. per l. of (NH₄)₂SO₄ in the electrolyte and deposition of the metal at 50 amp. per sq. ft. at pH 1.9-2.1. Stainless steel cathodes and Pb anodes proved satisfactory. Oxides of Co and Pb are deposited at the anode, especially at higher current density. Sodium and nickel sulfates accumulate in the electrolyte and must be removed periodically. Wetting agents aid in increasing efficiency of Co deposition. The fluoroborate electrolyte for electrowinning Co was tested successfully over a relatively long period of continuous operation.

162. SHIMIZU, MASAO, AND SUGIMOTO, TOMIZO. [Pure Iron, Magnesium Salt, and Pure Nickel From Serpentine.] Japanese Patent 755, Mar. 4, 1952; *Chem. Abs.*, vol. 47, 1953, p. 5342e.

Pulverized serpentine (100 kg.) containing 10-20 percent sand but no Ti, V, or P is mixed with 5 kg. calcium hydroxide and a suitable amount of water, about 10 percent of clay suspension is removed by decanting, and the residue is dried at room temperature; Fe sand (I) is separated by the use of a magnet, (I)

is reduced in an electric furnace with fluorite and carbon to give 8 kg. of Fe; the residue (60 kg.) after the separation of (I) is added to 15 liters of 66° B. sulfuric acid, heated in an autoclave for 2 hours at 30 p. s. i. pressure, diluted with water, filtered, and the filtrate is concentrated to give 5.8 kg. of magnesium sulfate of 99.8 percent purity. The residue (60 kg.) from the magnesium sulfate is treated with 17 liters of 66° B. sulfuric acid and 11 liters water, heated with superheated steam for 3.5 hours at 75 p. s. i., the product is filtered, the filtrate treated with ammonium hydroxide to pH 3.5-4.5, a small amount of sodium peroxide is added, air is bubbled in for 4 hours to precipitate hydrated ferric oxide, the precipitate is filtered, (gives 4 kg. rouge on heating), and the filtrate is concentrated to 30 liters and electrolyzed with addition of 10-20 gm. (NH₄)₂SO₄ to give 3 kg. Ni of 99-percent purity.

163. SIMPSON, K. M. Removing Nickel and Chromium From Iron Ore. U. S. Patent 2,199,654, May 7, 1940; Chem. Abs., vol. 34, 1940, p. 5815².

The ore is passed over slime tables while in finely divided form to separate minerals containing Cr. Ni in the ore is converted to metallic form, as by the action of reducing gases at 350°-550° C. Substantially all of the Fe is left in the oxide form, and the ore is treated further with CO to form nickel carbonyl vapors, which are separated.

164. TOBELMANN, H. A., AND MORGAN, H. J. Review of the Nicaro Nickel Project, Nicaro, Oriente Province, Cuba. Plancor 690, Jan. 15, 1948. Nicaro Nickel Project. Progress of Phases of Nickel Recovery in the Caron-Clevenger Ammonia-Leach Plant at Nicaro, Oriente Province, Cuba, 1941-46, 155 pp., 50 refs. Available from General Services Administration, Washington, D. C.

A complete pilot plant was erected at Hoskins Mound, Tex., by the Freeport Sulfur Co. to obtain vital information on key operations in the Nicaro Project. A 1-ton-of-ore-per-hour Herreshoff furnace was operated on a feed of roughly 2 parts laterite to 1 part altered serpentine to give about 90-percent reduction of the Ni. Other metallurgical operations, such as the leaching circuit, ammonia recovery, settling of tailings in Dorr thickeners, calcining of basic nickel carbonate to oxide, and temperature problems were piloted here also. The operation in the plant equaled pilot-plant figures, except for the reduction, which was a vital point. This is a comprehensive account of the wartime emergency plant operation, setting forth authorization measures and procurement of equipment and comparing performances of various metallurgical devices.

165. VENTURES, LTD. [Nickel Salts From Lateritic Ores.] French Patent 821,783, Dec. 13, 1937 (see U. S. Patent 2,105,456, Chem. Abs., vol. 32, 1938; p. 2302²); Chem. Abs., vol. 32, 1938, p. 3747².

NONOXIDIZED ORES

166. ASHCROFT, E. A. [Working Up Copper and Nickel Ores.] German Patent 585,697, Oct. 10, 1933 (Cl. 40a 2.50) (see British Patent 338,556, Chem. Abs., vol. 25, 1931, p. 2406); Chem. Abs., vol. 28, 1934, p. 2310².

167. ———. Treating Ores or Concentrates of Copper and Nickel, etc. British Patent 338,556, Aug. 20, 1929; Chem. Abs., vol. 25, 1931, p. 2406.

Material containing copper or nickel sulfides, or both, is treated with air or O₂ at 600° C. to convert the Cu and Ni to sulfate (without disturbing or rabbling the materials during the reaction). The heat of reaction is usually sufficient to maintain the temperature after

the reaction is started, and the charge may be covered by a thin layer of inert material. When Ni is present, FeSO₄ or FeCl₃ may be added with advantage. Most of the Fe present remains in the residue as oxide on leaching, together with sulfates of gangue materials such as CaSO₄. O₂ or air enriched with O₂ may be used to start or assist the reaction, and various other details and modifications of apparatus and procedure are described.

168. CANADIAN CHEMICAL PROCESSING. Strategic Metal Out of the North. Vol. 38, April 1954, pp. 52, 54, and 56; Metals Rev., vol. 27, No. 7, July 1954, p. 29 (119c).

The equipment, plant layout, and processing techniques at Canada's Cobalt Chemicals, Ltd., are discussed. Includes photographs and a flowsheet.

169. CANADIAN METALS. Strategic Metal Produced by New Cobalt Chemicals Plant in Ontario. Vol. 17, No. 5, May 1954, pp. 40, 42, and 44 (see also Canadian Min. Jour., vol. 75, No. 6, June 1954, pp. 70-72); Eng. Index, 1954, p. 206.

A plant was opened at Cobalt, Ontario, by Cobalt Chemicals, Ltd., for production of Co-based alloys containing 13 to 66 percent Co. The processing of concentrates is discussed. Co is used in armorplate for battleships and tanks, high-speed cutting tools, magnets, and other applications.

170. CIOCHINA, I. [New Possibilities as Regards Extraction of Some Metals From Their Sulfurous Ores.] Chim. et ind., vol. 36, 1936, pp. 898-900 (see Chem. Abs., vol. 30, 1936, p. 8120¹); Chem. Abs., vol. 31, 1937, p. 1736¹.

Laboratory samples of 5 gm. of various minerals of Cu, Ag, Ni, Pb, and Co, mostly sulfides, were subjected to heat treatment for virtually complete desulfurization. The temperature used and duration of treatments are reported for each mineral. It is stated that virtually pure Ni or Co can be obtained, and the treatment could probably be applied to flotation concentrates.

171. DEAN, R. S. Investigations on Nickel-Copper Ore. Bureau of Mines Rept. of Investigations 3419, 1938, p. 31.

The ore is in lenticular basic dykes in Precambrian gneiss and contains Cu, Ni, and Pt metals. It was intended to concentrate this ore by flotation and gravity methods, sinter the concentrates, and smelt the sinter in the electric furnace to produce crude anodes, which were to be refined electrolytically. Some small samples from the Key West mine were received. They were concentrated roughly by tabling and calcined. Analysis of the calcine is shown as SiO₂ 26.6, Al₂O₃ 5.8, Cu 3.3, Ni 5.2, Fe₂O₃ 23.8, CaO 7.8, MgO 10.9, and S 6.6 percent. The calcine was smelted in a tilting, carbon-resistance furnace with graphite crucible, a small amount of coal being used. Silica was added as a flux. Two mattes were analyzed: Matte No. 1 S 17.6, Fe 37.8, Cu 20.9, and Ni 22.9 percent; and matte No. 2 S 22.3, Fe 19.8, Cu plus Ni 58 percent. The electrolysis of the dissolved matte material does not appear in this report.

172. ———. Annual Report of the Metallurgical Division, Fiscal Year 1939. Bureau of Mines Rept. of Investigations 3480, 98 pp.; Chem. Abs., vol. 34, 1940, p. 5799¹.

Among other activities described, a low-grade nickel-magnesium silicate ore analyzing about 0.5 percent Ni was converted by steps into 98-percent electrolytic Ni. It was beneficiated by flotation to about 5 percent Ni, and a matte was made and converted, resulting in 28 percent Ni, which was then electrolyzed. The low-grade Nevada ore, analyzing Ni 0.51, Cu 0.52, Fe 9.63, MgO 22.0, and SiO₂ 39.0 percent, was floated; it gave a concentrate assaying Ni 4.66, Cu 6.12, Fe 25.85, S 17.63,

Mg 13.0, and SiO_2 21.2 percent. From this a matte was made assaying Ni 9.15, Cu 11.61, Fe 47.4, and S 32.4 percent. After converting, the white-metal anodes analyzed Ni 28.42, Cu 44.01, Fe 2.95, and S 21.75 percent. From this, electrolytic Cu (Cu 99.77, Ni 0.0008, Fe 0.0014, and Ag 0.00076 percent) and electrolytic Ni (Ni 98.68, Cu 0.038, Co 0.59, and Fe 0.15 percent) were produced.

173. DEAN, R. S. Recovery of Nickel From Ore Occurring at Bunkerville, Nev. Bureau of Mines Rept. of Investigations 3547, 1941, pp. 27-33.

The ore is first concentrated by flotation. A table shows the concentration of reagents fed, pounds of ore treated, and analyses of heads, tails, and concentrates. A flowsheet (stated to be much simpler than comparable Canadian process) indicates the detailed operation, which includes key operations of smelting, converting, electrolysis, and furnace refining for Cu, and smelting, converting to matte, electrolysis to remove Cu, solution purification, and precipitation of nickel carbonate with Na_2CO_3 , which is dissolved and electrolyzed to nickel cathodes, using Pb anodes for Ni recovery.

174. ———. Annual Report of the Metallurgical Division, 1941. Bureau of Mines Rept. of Investigations 3600, 1941, 70 pp. (see Chem. Abs., vol. 35, 1941, p. 3571²); Chem. Abs., vol. 36, 1942, p. 4069.

A satisfactory process has been developed for recovering Co electrolytically from complex domestic ores. From an ore containing approximately 1 percent Co_2O_3 and 0.5 percent Cu, a concentrate assaying Co_2O_3 14-15 and Cu 12 percent was obtained by flotation. Co was dissolved with aqueous SO_2 , with 98 percent extraction. After purification (described), $\text{Co}_2(\text{CO})_8$ was precipitated, then redissolved in H_2SO_4 and electrolyzed. Current efficiencies were 85-90 percent. A flowsheet is given.

175. DESBRIERE, G. [Cobalt at Haut-Katanga.] L'Industrie du cobalt dans le Haut-Katanga. Rev. mét., vol. 49, No. 11, November 1952, pp. 777-782.

The mining of Co ores, ore treatment, and reduction are described.

176. FORWARD, F. A. (assigned to Sherritt Gordon Mines, Ltd.). Extraction of Nickel Values From Nickeliferous Sulfide Material. British Patent 670,184, Mar. 28, 1949; Canadian Patent, June 11, 1948; British Abs., 1952, p. B-1-1145.

Nickeliferous sulfide ore, concentrate, or matte (Ni content 2-7 percent) is ground to 325-mesh in an atmosphere of O_2 , O_2 -enriched air, or air in the presence of aqueous NH_3 (28 percent) to produce a pulp with 80 percent of solids, which is then leached with aqueous NH_3 in a series of pachuca tanks at a pressure of about 30 p. s. i. The leach liquor is flash-boiled to remove most of the excess NH_3 and neutralized with H_2SO_4 to precipitate $\text{NiSO}_4(\text{NH}_4)_2\text{SO}_4$, which is filtered off. The filtrate is heated to 76°-93° C. to precipitate CuS . The filtrate from the CuS precipitate is neutralized with CaCO_3 , and Co is precipitated by addition of CaS .

177. ——— (assigned to Sherritt Gordon Mines, Ltd.). Extracting of Nickel Values From Nickeliferous Sulfide Material. U. S. Patent 2,576,314, Nov. 27, 1951; Chem. Abs., vol. 46, 1952, p. 1423c, d, e.

The finely pulverized ores or mattes, without previous conversion to oxides, are leached directly with a strong aqueous NH_3 solution, substantially free of carbonate, in the presence of air, O_2 -enriched air, or O_2 and with simultaneous agitation. The pressure of the oxidizing gases is preferably increased to 30 p. s. i. Some of the S appears in the elementary form and may be recovered by flotation, but most of it is transformed into sulfate and thiosulfate. Fe is precipitated as $\text{Fe}(\text{OH})_3$ and filtered off. The bulk of the Ni, Co, and Cu goes into solution and is recovered separately,

such as in the form of nickel ammonium sulfate, which may be converted to NiO by roasting. Leach solutions containing 70 to 95 gm. Ni per liter are obtainable. Previous processes utilizing ammonia, ammonium carbonate leach solutions require preliminary roasting of the sulfides to convert to oxides and the maximum Ni content obtainable in the leach solution is approximately 16 g./l.

178. ——— (assigned to Sherritt Gordon Mines, Ltd.). Extraction of Nickel Values From Nickeliferous Sulfide Material. British Patent 670,184, Apr. 16, 1952 (see U. S. Patent 2,576,314, Chem. Abs., vol. 46, 1952, p. 1423c); Chem. Abs., vol. 46, 1952, p. 7509f.

179. ——— (University of British Columbia, Canada). Ammonia Pressure Leach Process for Recovering Nickel, Copper, and Cobalt From Sherritt Gordon Nickel Sulfide Concentrates. Trans. Canadian Inst. Min. and Met., vol. 56 (in Canadian Min. and Met. Bull. 499, 1953, pp. 677-684) (see Chem. Abs., vol. 47, 1953, p. 7963h and vol. 48, 1954, p. 514d); Eng. Index, 1954, p. 758; Metals Rev., vol. 27, No. 1, January 1954, p. 36, (14-B).

Neither roasting nor smelting is involved. Air, NH_3 , water, steam, H_2 , and H_2S are the only reagents required in this wet chemical process. In this paper, no attempt is made to describe any of the details of the operation or to discuss the exhaustive tests made to determine the chemistry and operating characteristics of specific sections of the process. The process involves treating the Ni-Cu-Co-FeS₂ concentrates under pressure with air and NH_3 to dissolve the valuable metals and most of the S, leaving the Fe and other impurities in a tailing, which is discarded. The Cu is first separated from the solution as sulfide by a boiling operation, the Ni is then precipitated by H_2 under pressure, and the Co removed and purified; the end solutions are evaporated to product $(\text{NH}_4)_2\text{SO}_4$.

180. ——— (University of British Columbia, Canada). Sherritt Gordon Uses Ammonia Leach for Lynn Lake Nickel, Copper, Cobalt Sulfides. AIME, Min. Eng., vol. 5, No. 6, 1953, pp. 576-581; Chem. Abs., vol. 47, 1953, p. 7963h.

Starting with an ore containing about 1 percent Ni, a flotation process produces a concentrate assaying Ni 10-14, Cu 1-2, Co 0.3-0.4, Fe 33-40, S 28-34, and insoluble matter 8-14 percent with less than 0.2 oz. per ton of precious metals. The hydrometallurgical process employs successful dissolution of Ni, Cu, Co ore, or concentrate in ammonia and oxygen under pressure and without previous reduction to metal. Hydrated ferric oxide is formed and removed. Cu precipitated as sulfide, is shipped elsewhere for pyrometallurgy. Hydrogen under pressure precipitates metallic Ni and Co powders separately. Sulfur compounds are converted to ammonium sulfate, which is sold. Equations representing the reactions and a flowsheet are given.

181. ——— (University of British Columbia, Canada). Production and Properties of High-Purity Nickel Powder. Jour. Inst. Metals, vol. 82, 1954, pp. 113-116 (paper B-7); Chem. Abs., vol. 48, 1954, p. 7516c; Eng. Index, 1954, p. 713.

A Ni concentrate containing Ni 10-16, Cu 1-2, Co 0.2-0.4, Fe 30-40, S 28-34, and SiO_2 8-14 percent is refined by NH_3 leaching in horizontal autoclaves under a pressure of approximately 100 p. s. i. to (1) dissolve Ni, Co, and Cu as amines; (2) oxidize S to sulfate, thiosulfate, thionate, and sulfamate ions; (3) precipitate Fe as Fe_2O_3 ; and (4) remove SiO_2 and insoluble materials by filtration. The amine liquor is (5) boiled to decompose thionates and convert Cu to CuS which is removed by filtration, leaving Cu at less than 0.005 g. per l. The Ni-Co solution containing Ni 45 and Co 0.7 gm. per l. is (6) heated in a mechanically stirred

autoclave at 175° C. to 230° C. with compressed air to remove $(\text{NH}_4)_2\text{SO}_4$ and form $\text{Ni}(\text{NH}_3)_4\text{SO}_4$, which is reduced by H_2 to precipitate Ni. Control of this last operation leaves most of the Co in solution.

182. FORWARD, F. A. (assigned to Sherritt Gordon Mines, Ltd.). Recovery of Nickel From Nickel Ores. British Patent 715,243, Sept. 8, 1954; U. S. Patent 2,616,781, Nov. 4, 1952; Chem. Abs., vol. 47, 1953, p. 2114i; Chem. Abs., vol. 49, 1955, p. 2285h.

Ni ores containing Cu and Fe are ground to about 100-mesh and roasted at 500°–800° C., and the roasted calcine is reduced with H_2 at 480°–525° C., higher temperatures causing an excessive reduction of Fe, in a closed reduction chamber and preferably with the addition of about 5 percent powdered coke, which reduced H_2 consumption from 4,000–5,000 cu. ft. per ton to 1,300 cu. ft. per ton. The reduced calcine is mixed with 3 parts NH_3 – $(\text{NH}_4)_2\text{CO}_3$ leaching solution, heated to 35°–40° C., and O_2 or oxygenated air is passed through the pulp until all Fe is converted to $\text{Fe}(\text{OH})_3$. Then the pulp, containing 5 percent solids, is leached at 30°–50° C. with a leaching solution agitated with a stream of O_2 and NH_3 , preferably in 2 stages. From the filtrate Cu is separated by adding Ni powder, filtering off, and the Ni precipitated as NiCO_3 by boiling.

Recovery of about 90 percent of the Ni is reported.

183. FORWARD, F. A., AND LYLE, A. G. Recovery of Cobalt, Copper, and Gold From Arsenical Concentrate by Roasting and Leaching. Bull. Inst. Min. Met. (London), No. 470, 1945, pp. 16–18; Chem. Abs., vol. 39, 1945, p. 1121¹.

A concentrate containing Au 1.05 oz. per ton and Co 0.88, Cu 0.65, As 39.3, S 19.0, Fe 32.0, and insol. 4.7 percent, produced by floating cyanide tails, was heated rapidly to 800° C. and held until evolution of As fumes ceased. The calcine was cooled to 500° C. with a minimum access of air. It was roasted at 500°–550° C. with controlled air for approximately 1½ hours. The temperature was raised to 650° C. to decompose FeS_2 . The sulfated calcine was leached 20 minutes in warm H_2O , which extracted 75–90 percent of the Co and 40–60 percent of the Cu. By addition of 1 percent H_2SO_4 , extraction of Co and Cu was 95 percent. Co and Cu can be precipitated. Au can be recovered by cyanidation of the residue.

184. FORWARD, F. A., SAMIS, C. S., AND KUDRYK, V. (University of British Columbia, Canada). A Method for Adapting the Ammonia Leaching Process to the Recovery of Copper and Nickel From Sulfide Ore and Concentrate. Trans. Canadian Inst. Min. and Met., vol. 51, 1948, pp. 350–355, in Canadian Min. and Met. Bull. 434; Chem. Abs., vol. 42, 1948, p. 6286g.

If the concentrate is roasted to remove S, the calcine can be reduced with H_2 at 900° F. to give a product in which the Ni and Cu are chiefly in metallic form, but Fe is mostly present as Fe_3O_4 . The amount of H_2 consumed varies from 1,000 cu. ft. per ton for low-grade sulfide concentrate of ore to 6,000 cu. ft. per ton of 17 percent Ni concentrate. The inhibiting effect of the reduced Fe on Ni solution can be overcome by gently stirring a 30-percent pulp containing reduced calcine and NH_3 leaching solution for 30–60 minutes at 100° F. in contact with an O_2 atmosphere. Ninety-five percent of the Ni and 80–85 percent of the Cu can be extracted from concentrate containing 17 percent Ni and 1.7 percent Cu by leaching the reduced, digested calcine with NH_3 – $(\text{NH}_4)_2\text{CO}_3$ solution in a 5-percent pulp at 80° F. for 2 hr. If O_2 is used for agitation of the leach. The dissolved Cu can be precipitated from the NH_3 leach solution by cementation with reduced Ni if mechanically agitated at 150° F. for 30 minutes, excluding air. During the cementation period any traces of ferrous Fe

that may be in the leach solutions are oxidized, precipitated, and removed from the solution with the cement Cu; this leaves a final purified Ni-ammonium solution completely free of Fe and substantially free of Cu.

185. GILL, J. R., AND CRAIG, E. Nickel-Copper Smelter at Falconbridge. Trans. Canadian Inst. Min. and Met. (in Bull. 243), 1932, pp. 315–322; Min. Jour. (London), vol. 178, pp. 599–600; Chem. Abs., vol. 26, 1932, p. 5520.

Describes the Falconbridge plant. The coarse ore is smelted in a blast furnace. The necessary basic flux is furnished by converter slag plus enough limestone to give 5–6 percent CaO in the furnace slag. The low-grade matte produced (9.5–11 percent Ni and Cu) is blown in a converter to almost complete removal of Fe (less than 0.2 percent); fine ore is used to provide the necessary SiO_2 for fluxing.

186. INTERNATIONAL NICKEL CO. Inco Tells What It Takes to Open Up New Ore Body. Eng. and Min. Jour., vol. 152, No. 11, November 1951, pp. 96–98 (see Canadian Metals, vol. 15, No. 4, April 1952, pp. 22–23); Eng. Index, 1952, p. 676.

A new shaft and concentrator have been completed at the Creighton mine in the Sudbury district. The mill capacity is 10,000 tons of ore daily, with the primary crushing of ore accomplished underground. Flotation process uses 144 mechanical-type cells. The water supply, dust control, electrical service, and automatic sampling are discussed. The sinking of No. 7 shaft is described.

187. JOURNAL DU FOUR ÉLECTRIQUE. [The Metallurgy of Cobalt at l'Union Minière du Haut Katanga.] Vol. 62, 1953, pp. 18–21. Chem. Abs., vol. 47, 1953, p. 4265f.

The metallurgy is described in flowsheet style from flotation to granulated Co metal. An electrolysis deposits out Cu, leaving Co in the slimes. Partial separations of the elements from the slimes are then made by multistep neutralizations with lime. Further electrolysis produces metal containing about 93 percent Co, which is refined in an electric furnace, granulated in water and screened.

188. KENWORTHY, H., AND KERSHNER, K. K. Metallurgical Investigations of Southeastern Missouri Cobalt-Nickel Resources. Bureau of Mines Rept. of Investigations 4999, 1953, 37 pp.; Chem. Abs., vol. 48, 1955, p. 515b.

Sulfide ore concentrates containing Co, Ni, Cu, Pb, and Fe from the National Lead Co. at Fredericktown, Mo., were chlorinated on a laboratory scale with gaseous HCl to form anhydrous metal chlorides and sulfur chlorides. Sulfur chlorides were removed by distillation, a high percentage of the Fe was converted to ferric oxide, and the chlorinated residual metals were extracted with H_2O . Metal ions were removed from leach liquors by pH-controlled fractional precipitation as hydroxides. Co solutions prepared by dissolution of the cobaltic hydroxide were freed of contaminating metal ions, and used as electrolytes for deposition of high-purity Co.

Co-Ni-bearing pyrite concentrate was given a partial roast at low temperatures to oxidize the pyrite surfaces. The roasted material was then floated to produce a high Co-Ni concentrate containing over 80 percent of the Co and Ni and about 10 percent of the Fe. Complex Cu-Pb-Co-Ni-Zn-Fe matte from the St. Joseph Lead Co. at Herculaneum, Mo., was treated in a laboratory converter to remove most of the Pb and Zn as fume and to slag over half of the Fe. The enriched, S-deficient matte was then treated by crystallization and subsequently by flotation or by magnetic separation to yield a high-Co-Ni and a high-Cu product.

189. KIYOKADO, NISHIHARA, KONDO, YOSHIO, AND SAKO, HIDEKI. [Treatment of Copper- and Cobalt-Bearing Pyrite.] *Kyoto Univ. Bull. Inst. Chem. Research*, vol. 32, 1954, pp. 95-96; *Chem. Abs.*, vol. 49, 1955, p. 2271c.

Using a Co-bearing pyrite containing Fe 37.34, Cu 3.71, Co 0.31, and S 42.76 percent, the recovery of Cu and Co was found to be much easier by roasting and leaching than by pyrometallurgy. With oxidizing roasting in a rotary kiln at 550° C. to 2.5 percent S and leaching in a sample jar rotating at 120 r. p. m., the recoveries were Cu 79, Co 84, and Fe 5 percent.

A chloridizing roast of a cinder containing 10 percent S, followed by a leach, showed 95 percent Cu and 90-98 percent of Co recovery, with a smaller content of Fe than in the first trial.

190. KOSTER, J., KNICKERBOCKER, R. G., GARST, O. C., EVANS, T. E. AND CODY, W. E. Recovery of Nickel, Copper, and Precious Metals From Domestic Ores by a Combined Electrothermal and Electrolytic Method. Bureau of Mines Rept. of Investigations 3483, 1939, 28 pp.; *Chem. Abs.*, vol. 34, 1940, p. 3181²; *British Chem. Abs.*, 1940, p. B-452.

Starting with a sulfide ore containing 0.5-1.5 percent Ni the following operations were tried: (1) Selective flotation, increasing the Ni to 5 percent; smelting to a matte, increasing Ni to 9.0 percent; fluxing with quartz and obtaining an alloy containing 28 percent Ni; finally electrolysis plated out Cu faster than Ni, enriching the solution in Ni; further electrolysis removed all but a small amount of Cu, which was cemented out; after removal of Fe, Ni was precipitated as basic carbonate partly, and pure electrolytic Ni produced from a solution. Precious metals were recovered.

191. LEMAIRE, EUGENE. [Treatment of Petsamo Nickel Ore.] *Ind. chim.*, vol. 36, No. 382, 1949, pp. 95-96; *Chem. Abs.*, vol. 43, 1949, p. 6955d.

The Finnish Lapland ore, which has yielded 350,000 metric tons of mineral per year up to 1939, is similar to the Sudbury deposit, being both nickeliferous and cupriferous. The reddish tinged, light-bronze-colored magnetic pyrite has the formula $\text{FeS} \cdot \text{Fe}_2\text{S}_3$. Refined matte containing Ni 23, Cu 15, Fe 37, and Si 20 percent was prepared in 4 electric arc furnaces at Petsamo and then sent to the I. G. Farbenindustrie at Oppau, Germany, where, under a pressure of 200 kg. per sq. cm. (which is finally reduced to 21 kg. per sq. cm. and 250° C.), 85 percent of the Ni was transformed to volatile $\text{Ni}(\text{CO})_4$, and a fraction of the Fe to volatile $\text{Fe}(\text{CO})_5$. After liquefaction under pressure, the 2 carbonyls were fractionated under a reduced pressure of 0.5 kg per sq. cm. at 80° C. (boiling point of $\text{Fe}(\text{CO})_5$ = 103° C. and of $\text{Ni}(\text{CO})_4$ = 43° C.). The $\text{Ni}(\text{CO})_4$ is decomposed at 220°-240° C. under a pressure of 0.2 to 0.4 meter of water, depending on the fineness of the Ni powder desired. The Oppau residue containing 70 percent Cu, 3 to 4 percent Ni, and the precious metals, 5 gm. per metric ton Au, 15 gm. per metric ton Pt, and Pd was formed into anodes for the recovery of Cu by electrolysis.

192. LUTJEN, G. P. Cobalt at Fredericktown. *Eng. and Min. Jour.*, vol. 154, December 1953, pp. 72-76; *Metals Rev.*, vol. 27, No. 2, February 1954, p. 37 (22-B); *Chem. Abs.*, vol. 48, 1954, p. 5755f.

The new refinery at Fredericktown, Mo., will be the first in the United States to adapt the Chemico process to an existing mill operation. The present mill processes 1,350 tons of ore per day, containing Pb 2.5-2.75, Cu 0.5-0.75, Ni 0.25, Co 0.25, and Fe 5-6 percent. Pb, Cu, Ni, and Co are recovered in a bulk-flotation concentrate. After selective recovery of Pb and Cu from the bulk concentrate, tailing from the Cu flotation contains about 2 percent each of Ni and Co. Previously discarded, this tailing will be ammonia

leached and oxidized at 1,000 p. s. i. in the new refinery to recover Ni and Co.

193. MCGAULEY, P. J. (assigned to Chemical Construction Co.). Recovery of Complex Ammonium Sulfates From Mineral Leach Liquors. U. S. Patent 2,647,819, Aug. 4, 1953; *Chem. Abs.*, vol. 47, 1953, p. 10448b, d.

Cu and Co are recovered from concentrates, which may also contain Ni and Fe, by leaching with H_2SO_4 or an ammoniacal liquor, and filtering. The pH of the filtrate is adjusted to 3-4 to precipitate $\text{Fe}(\text{OH})_3$, which is removed, increasing the pH to 4-6.4 to precipitate a nickel-ammonium sulfate, increasing the ammonium-salt concentration to about 40 percent at a pH of about 5.5 to precipitate Co as a complex ammonium sulfate; and increasing the ammonium-salt concentration to precipitate Cu as a complex ammonium sulfate.

194. MINING WORLD. "Sweat, Ingenuity, Dollars," A New Mine for Howe Sound. Vol. 13, Nov. 1951, pp. 40-43; *Metals Rev.*, vol. 25, No. 1, January 1952, p. 20 (7B).

The Calera Mining Co. has carved a Co and Cu producer from Idaho's Salmon National Forest. Discusses procedures in recovering Cu and Co.

195. MOND NICKEL CO. Treatment of Sulfide Ores Containing Nickel. British Patent 659,283, Oct. 17, 1951; *Chem. Abs.*, vol. 46, 1952, p. 4459h; *British Abs.*, 1952, p. B-1-249.

By successive roasting and preferential reduction of a nickeliferous pyrrhotite concentrate, it is possible to obtain a mixture of nickel and iron oxides that can be resolved by ammoniacal leaching into separate Fe and Ni portions. The concentrate is first reduced to about 200-mesh and roasted at a temperature lower than the fusion temperature (generally 650°-870° C.) to convert the ore to the oxide. This produces a porous mass of oxides which are readily permeable by the reduction gases in the next step. The NiO is then reduced at 760°-870° C. in a reducing atmosphere of CO , H_2 , CO_2 , and H_2O such that a ratio of $\text{CO} + \text{H}_2\text{O}$ to $\text{CO} + \text{H}_2$ lies between 1.5 : 1 and 3 : 1. The FeO is substantially unaffected by this treatment. An ammoniacal leach is then carried out in the usual fashion to dissolve the Ni from the Fe. The Fe ore left is suitable for use in steel manufacture, while the Ni is pure enough for further use in purification.

196. NAKABE, SANAI (Besshi Mining Co., Ltd., Tokyo). [Metallurgy of Cobalt Production From Cupriferous Pyrite.] *Jour. Metals*, vol. 3, 1951, pp. 445-451; *Chem. Abs.*, vol. 45, 1951, p. 6134g.

Japanese wartime economy demanded domestic Co production. This paper describes a process operated for 2 years at the Besshi mine and smelter on extremely low grade (0.1 percent Co) pyrite concentrates obtained from Cu ore. The steps in this process were roasting, leaching, precipitation, reduction to crude Co, and finally refining by electrolysis to 99+ percent Co.

197. O'DEEN, G. A., AND OTHERS. [Simultaneous Recovery of Metals and Sulfur From Metal Sulfides.] Norwegian Patent 83,374, Mar. 22, 1954; *Chem. Abs.*, vol. 48, 1954, p. 8159f.

Sulfide ores are heated with C and CaO or Na_2CO_3 in an atmosphere of CO to a temperature at which the metal produced is in a molten condition. CaF_2 or CaCl_2 is used as a flux in an amount sufficient to give a fluid CaS or Na_2S slag. The slag is treated with steam and CO_2 to recover the S and alkali, for example, by boiling the slag in water while passing in CO_2 . In an example, pyrites are heated to drive off S, and the residual FeS is heated with CaO , CaF_2 , and C in an electric furnace to give Fe, CaS - CaF_2 slag, and CO . The slag is then treated with steam and CO_2 to give CaCO_3 , CaF_2 , and H_2S . The H_2S is passed with air over an Fe_2O_3 or bauxite catalyst to give S in 85-percent yield. A complex pyrite is heated to drive off S and

As₂S₃ and smelted with CaO, CaF₂, and C. Zn distills off, and Fe, Ni, and Co are tapped from the bottom of the furnace.

198. RUTLEDGE, F. A. Exploration of Red Mountain Chromite Deposits, Kenai Peninsula, Alaska. Bureau of Mines Rept. of Investigations 3885, 1946, 26 pp.; Chem. Abs., vol. 40, 1946, p. 4631².

A test on an ore containing Cr₂O₃ 28.2, Fe 7.7, and SiO₂ 19.2 percent recovered 89 percent of the Cr in a concentrate containing Cr₂O₃ 45.1 percent and SiO₂ 11.4 percent. Finer regrinding of middlings increased recovery and lowered the grade slightly. Flotation was unsuccessful. Magnetic concentration alone recovered 74 percent of the Cr in a product containing 43.4 percent Cr₂O₃. Combined magnetic and table concentration yielded a product containing 39.1 percent Cr₂O₃ at 96.9-percent recovery. A composite of gravity rejects containing Ni 0.24 percent was smelted with 10 percent coke in an electric-arc furnace to give a metallic button containing Fe 70.2 percent, Cr 5.04 percent, and Ni 2.4 percent.

Various leach solutions were tried on the ore. Only stage leaching with HCl showed promise. In a 2-stage HCl leach, 80 percent of the Ni was recovered in a Ni-Fe product. However, in the 3-stage leaching with hydrochloric acid, 85 percent of the Ni could be accounted for in the combined Fe and Ni precipitates. A Ni precipitate was prepared that contained 52.5 percent of the Ni.

199. SCHWELLENUS, C. M. The Nickel-Copper Occurrence at the Bushveld Igneous Complex West of the Pilandsbergen. Union of South Africa, Dept. Mines, Geol. Series Bull. 5, 1935, 36 pp.; Chem. Abs., vol. 30, 1936, p. 57⁴.

The source, grade, treatment, and use of these ores are discussed.

200. SIMPSON, K. M. Recovery of Nickel From Ores. U. S. Patent 2,254,158, Aug. 26, 1941; Chem. Abs., vol. 35, 1941, p. 7927¹.

The arrangement of apparatus used is described. The process involves converting the Ni of an ore to metallic Ni, as by the action of producer gas at 975° F., and then treating the ore, while it contains at least 15 percent of moisture, with CO to produce substantially pure nickel carbonyl, and thereafter decomposing the nickel carbonyl to obtain substantially pure Ni.

201. STAHL, J. C., AND SHELTON, F. K. Cobalt Salts From Arseniferous Cobalt Ores. U. S. Patent 2,526,707, Oct. 24, 1950; Chem. Abs., vol. 45, 1951, p. 13111.

A comprehensive report of laboratory investigations is presented, directed toward the best conditions for producing Co salts from As-containing concentrates.

Reducing roasting, provided that the temperature does not exceed 550°–700° C., forming ferrites, can safely remove some As. The 89.1 percent of As remaining is eliminated by adding 40 parts of S to 50 of calcine and roasting for 2 hours at 850°–900° C., preferably at a particle size of 10-mesh or finer. The calcines are first leached in cold 10-percent H₂SO₄ and then in hot 20-percent for a maximum Co extraction.

At pH 1.2–1.7 cobalt arsenite precipitates from cold solutions.

202. TALBOT, H. L. Investigations on the Production of Electrolytic Cobalt From a Copper-Cobalt Flotation Concentrate. Bull. Inst. Min. Met., No. 514, 1949, pp. 1–19; Chem. Abs., vol. 43, 1949, p. 8996g.

The two processes described have a particular application for the recovery of Co from sulfide concentrates of relatively low Co content and high Fe:Co ratio. Laboratory and pilot-plant experiments were made on Rhokana flotation concentrate. In the matte-

leach process the concentrate was smelted to matte, from which the Co was leached with H₂SO₄ and recovered by electrolysis from the purified solution. In the roast-leach process the concentrate was roasted and the Co extracted from the calcine by leaching with hot H₂O, after which the Co was recovered from the purified solution by electrolysis.

203. UDRY, M. J. Metallurgy. British Patent 566,375, Dec. 28, 1944; Chem. Abs., vol. 41, 1947, p. 679e.

Ore containing Fe in various combinations with Ni, Cu, and Co is smelted with a suitable fluxing material to produce a matte containing the sulfides of the metals, which is soluble in a mineral acid, such as H₂SO₄, and a separable slag containing the gangue materials of the ore. The matte is separated from the slag and digested with acid, to separate Fe from the other metals. Treatment of the matte with an aqueous solution of H₂SO₄ will produce H₂S, an aqueous solution of FeSO₄, and a solid product containing the sulfides of Ni, Co, and Cu, together with any precious metals that may be present in the ore. The slag is disposed of in any suitable manner.

204. VOGEL, F. [A New Path in the Metallurgy of Nickel-Copper Separation.] Metallbörse, vol. 19, 1929, pp. 1601–1602; Chem. Abs., vol. 23, 1929, p. 5135⁴.

The older separations of Cu and Ni by smelting them to high-grade mattes, either with or without the use of alkali sulfides, and then leaching with H₂SO₄, are compared with the Mond process (separation as Ni (CO)), from reduced Ni and Cu) and a new process (Canadian Patent 279,756), with commendation for the last named. It involves concentrating to a matte containing 2–5 percent Fe, granulating in water, grinding to 80-mesh, dissolution of 99.0–99.9 percent Ni and Fe in hot 30-percent H₂SO₄, removal of Fe by use of Ni (OH)₂, recovery of NiSO₄, decomposition into NiO by heat, smelting to Ni in a reverberatory furnace, using petroleum-retort coke as a reducing agent. The complete separation of noble metals from Ni is a valuable factor.

205. WALDRON, H. L. Sherritt Gordon Develops Lynn Lake Nickel-Copper. Eng. and Min. Jour., vol. 152, Nov. 1951, pp. 72–78; Metals Rev., vol. 24, December 1951, p. 26 (285–B).

Geology, use of electromagnetic surveying, new ores discovered, and new methods of concentration are discussed.

Basically, the process consists of simultaneous oxidation and ammonia leaching of the concentrates to produce soluble Ni, Co, and Cu compounds. Ni and Co are recovered in powder form. The advantages as opposed to conventional methods are low operating costs, high recovery of pure Co, and 75-percent recovery of S as ammonium sulfate.

206. WHITTMAN, J. [Electrometallurgical Production of Cobalt and Copper in the Belgian Congo.] Jour. du four électrique, vol. 56, 1947, No. 4–5, pp. 55–56; Chem. Abs., vol. 42, 1948, p. 1133d; vol. 44, 1950, p. 6741e.

The Co concentrates, scoria, and dross are fed into an electric arc furnace, and lime and coke are added. The furnace is a single-phase Girod type, 6 ft. in diameter. The product is a white alloy containing Fe, Cu, Si, and about 42 percent Co. It is granulated in water. The heavy Cu granules are cast into red ingots carrying a trace of Co; these are refined in a rotating furnace. The scoria, containing 17 percent Co, is returned to the arc furnace. The electrolytic refining of Co involves a series of operations to eliminate the Fe and Cu. Salts of Co are selectively precipitated by the action of added CaO. The hydrated Co precipitate is dissolved in a weak acid. The Co is electrolytically deposited on Fe plates, from which it is readily

stripped. This Co metal is then fed into a 3-phase Lectromelt furnace (1,600 kv.-a.) and refined, cast, and granulated.

BENEFICIATION OF MATERIALS

ORE DRESSING; NONSPECIFIED ORES

207. ANDERSON, A. K. Concentration of Copper-Nickel-Bearing Gabbro From Engineers Holding Co., Michipicoten, Ontario. Canadian Dept. Mines, Mines Branch Rept. 720, 1931, pp. 6-8; Chem. Abs., vol. 25, 1931, p. 3938.

The ore analyzed Cu 1.23, Ni 0.51, Zn 0.14 percent, and Au 0.01, Ag 0.25, and platinoids (chiefly Pd) 0.06 oz. per ton. A bulk flotation yields high recoveries of Cu (98 percent), a large percentage of Ni (76.5 percent), and major amounts of the precious metals (Au 59, Ag 96, and platinoids 34 percent).

208. DEAN, R. S., AND DAVIS, C. W. Nickel (Magnetic Separation). Bureau of Mines Bull. 425, Magnetic Separation of Ores, 1941, 417 pp., p. 302; 371 refs.

Magnetic pulleys are used to remove concentrates at the Creighton mine of the International Nickel Co. 11 miles west of Sudbury, Ontario, and high-intensity magnetic separators are used in the plant of the Falconbridge Nickel Co., Falconbridge, Ontario.

209. ———. Theoretical Physical Basis of Magnetic Separation Processes. Relation of Electron Structure to Ferromagnetism for the Elements. Bureau of Mines Bull. 425, Magnetic Separation of Ores, 1941, pp. 19-22 (371 refs.).

In certain states of combination, elements 24 to 28, (Cr, Mn, Fe, Co, and Ni) are ferromagnetic. Physicists have postulated that, in addition to unbalanced electron spins, the resultant spins in neighboring atoms must be parallel. To meet this requirement, the diameter of the atom must bear the correct ratio to that of the electron shell in which the electrons are uncompensated. According to Slater, D/r must be greater than 3 for ferromagnetism. This explains the lack of ferromagnetism in Ti, Cr, Mn, Pd, and Pt but indicates that the rare earths are magnetic. Recent work also points to this conclusion.

210. DOREMAN, J., AND JAANUS, R. (Physical-Technical Laboratory, Leningrad-Sosnovska). [The Role of Conductivity Electrons in Ferromagnetism.] Naturwissenschaften, vol. 16, 1928, p. 1026; Chem. Abs., vol. 23, 1929, p. 1568¹.

From the magnetomechanic behavior of ferromagnetic substances it is probable that the spin moment, not the orbital momentum of the electrons, causes ferromagnetism. The authors endeavor to decide whether it is due to the free conductivity electrons or to the electrons bound in the positive metal ion. They conclude that the free electrons cause ferromagnetism, and preliminary data indicate that the same conclusion holds for Fe and Co.

211. GALPERIN, F. M. [Atomic Magnetic Moments of Iron, Cobalt, and Nickel.] Compt. rend. Acad. Sci., U. R. S. S., vol. 52, 1946, pp. 211-213; (see British Abs., 1946, p. A-1-307); British Abs., 1947, p. A-1-74.

By analogy between Slater's (British Abs., 1936, p. A-1055) and Galperin's (cited above) criteria for the occurrence of ferromagnetism, it is deduced that only when the distance between neighboring atoms in the lattice is the effective distance D , do the d -electrons of the atom take no part in the formation of interatomic bonds. D is defined as the sum of the radii corresponding to the maximum radial densities of electron charge of the s and d shells of the atom. At this distance the

atomic magnetic moments will have maximum values M , assumed to be 3, 2, and 1 Bohr magnetons per atom for Fe, Co, and Ni, respectively. By comparison of the values of M with D for the different atoms, an expression for the variation of atomic moment with interatomic distance is obtained, and the values are calculated for Fe, Co, and Ni from the known interatomic distances in the crystal. These are of the same order as experimental values for the atomic magnetic moment.

212. IWASE, KEIZO (Research Institute for Metals). [Selection of Nickel-Cobalt-Iron Oxide Ore.] Japanese Patent 176,413, June 26, 1948; Chem. Abs., vol. 45, 1951, p. 4633f.

Fe, Co, and Ni ores are pulverized and heated with salt at 700° C. for 20 to 30 minutes, which induces nonmagnetic properties in the Fe and Ni but tends to magnetize the Co, which is then separated magnetically.

213. MICHELL, F. B. The Dressing of the Lesser Metallic Minerals. Mine & Quarry Eng., vol. 13, 1947, pp. 300-305 and 334-342; Chem. Abs., vol. 42, 1948, p. 2898h.

Discusses dressing of ores of Al, Sb, Bi, Co, Cr, Mn, Mg, Hg, Mo, Ni, Ta, Th, Ti, U, and V.

214. ORTLEPP, J. A. L. Notes on the Nickel and Copper Deposits in the Norite Complex West of the Pilansberg District, Rustenberg, Transvaal. Jour. Chem. Met. Min. Soc. South Africa, vol. 29, 1929, pp. 233-236; Chem. Abs., vol. 23, 1929, p. 4425⁹.

In a discussion of Schoch's paper (Chem. Abs., vol. 23, 1929, p. 2910), Ortlepp gives certain results of assays and concentration tests on similar ore.

215. PARSONS, C. S., ANDERSON, A. K., JOHNSTON, J. D., AND JENKINS, W. S. The Concentration of the Disseminated Copper-Nickel Ore of the Falconbridge Nickel Mines, Limited, Falconbridge, Ontario. Canadian Dept. Mines, Mines Branch Rept. 736, 1934, pp. 171-185; Chem. Abs., vol. 28, 1934, p. 6404⁹, and vol. 29, 1935, p. 86⁹.

Highest recoveries were obtained in a soda-ash circuit. Good recoveries were obtained with lime and cement as alkaline reagents. A heavy oil mixture showed advantage over chemical collectors. Xanthates were necessary for low tailings. Mill recoveries of Cu were 90 percent and of Ni 98 percent. Reagent consumption was soda ash 0.20-0.30, xanthate 0.15-0.25, and Yarmor pine oil 0.05-0.15 lb./ton ore.

216. RANG, N. B. E. (assigned to Rang, A. B. C.). [Separation of Copper, Nickel, and Cobalt Ores.] Swedish Patent 86,547, June 16, 1936; Chem. Abs., vol. 30, 1936, p. 8136¹.

Magnetic ores containing Cu, Ni, or Co minerals are pulverized and classified, and one or more of the classes of powdered ore obtained is subjected to magnetic separation.

217. SIMONOV, K. A., AND DUIMOV, A. M. [Experiments on Dressing Khalilovsk Nickel Ore.] Tsvetnyye Metal, 1931, pp. 454-460; Chem. Abs., vol. 27, 1933, p. 482.

Ni ore having the composition Ni 1.44, Fe₂O₃ 22.19, SiO₂ 43.55, Cr 0.88, Al₂O₃ 3.42, MgO 3.25, S 0.14, and CaO 1.25 percent was treated by flotation and also by leaching with HCl and H₂SO₄ solutions at various concentrations. The best results are obtained by acid extractions. A 15.6-percent HCl solution gave 85.5-percent extraction, and 20.26-percent H₂SO₄ solution gave 77.5-percent extraction.

218. TIMM, W. B., AND OTHERS. Investigations in Ore Dressing and Metallurgy, July to December, 1933. Canadian Dept. Mines, Mines Branch Rept. 744, 1934, 194 pp.; Chem. Abs., vol. 29, 1935, p. 6862⁵.

Reports details on concentration and extraction tests of Cu-Ni ores.

219. WALLI, E. J., RYAN, J. P., AND SMITH, D. A. G. The Eldorado Operation at Great Bear Lake. *Trans. Canadian Inst. Min. Met.*, vol. 41 (in Canadian Min. Met. Bull. 310, 1938, pp. 61-76); *Chem. Abs.*, vol. 32, 1938, p. 2477¹.

Discusses the three phases of mineralization and marked surface alterations. Co and Ni minerals increase with depth and may assume importance. Flow-sheets for mineral concentration are presented, including screening, jigging, tabling, classifying, and flotation. Products include pitchblende, Co-Ni minerals, and Cu-Ag concentrate.

ORE DRESSING; OXIDIZED ORES

220. BINYON, E. O. Gibellini Manganese-Zinc-Nickel Deposits, Eureka County, Nev. Bureau of Mines Rept. of Investigations 4162, 1948, pp. 5 and 6.

This is an extremely complex ore carrying values of Mn, Fe, Ni, Co, Zn, Cu, Mo, V, and Ca; all these metals, however, appear to be carried by psilomelane, pyrolusite, and chalcodonic quartz. The ore, crushed to -20-mesh, washed, and screened and subjected to magnetic separation gave recoveries of 80 percent of the Mn, 71 percent of the Ni, 70 percent of the Zn, 79 percent of the V, 75 percent of the Co, and 74 percent of Mo. Previous work submitted by the owners of the ore showed that further beneficiation by gravity or flotation methods gave only a 60-percent Mn recovery in a product that would sinter to 44 percent Mn. Since the ultimate recovery of auxiliary metals would mean the introduction of hydrometallurgical methods, no further ore dressing was done. A few preliminary leaching tests were conducted after reducing roasts. By leaching with H₂SO₄, 64 percent of the Ni was recovered; however, by regrinding the ammonia leach residues and leaching with H₂SO₄, 89 percent of the Ni and 73 percent of the Co were recovered.

221. CANADIAN DEPARTMENT OF MINES, MINES BRANCH. Nickel-Copper Ore From the Gersdorffite Property Near Worthington, Ontario. Rept. 743, 1934, pp. 113-116; *Chem. Abs.*, vol. 29, 1935, p. 2486⁴ and 3267⁹.

The ore assayed 2.66 percent Ni, 0.16 percent Co, and 1.28 percent Cu, with values of precious metals.

Alteration of the Ni ore makes it difficult to obtain a bulk concentrate high in Ni; best results were had by using a distinctly alkaline pulp by potassium xanthate and by fine grinding.

222. CARPENTER, R. D. Mineral Beneficiation by Gravity Concentration, a Fundamental Study. University of Idaho, Moscow, Idaho, Idaho Bureau of Mines and Geol. Pamph. 84, 1949, pp. 1-16; *Chem. Abs.*, vol. 44, 1950, p. 2421i.

Gravity-concentration tests were made on an artificial magnetite-magnesite mixture, and on a natural Co-Cu ore by feeding a rotary pan concentrator on smooth, riffle, and rough surfaces, at various speeds of rotation. Rates of feed, pulp density of feed, particle size of feed, and surface slope were varied. A rotary pan gives a better recovery than a Wilfley table, especially in the minus-200-mesh sizes.

223. DAVIS, C. W., AND STAFF, METALLURGICAL DIVISION. Flotation Tests of Ores Requiring Sulfidization. Bureau of Mines Rept. of Investigations 3370, 1938, pp. 98, 99, and 101.

Laboratory tests in which valuable minerals are recovered by sulfidization during flotation are subject to difficulties at several points in the treatment.

The ore contained stainerite, a cobalt oxide mineral, and also cuprite, chrysocolla, and malachite. Previous work had shown that sodium sulfide as a sulfidizing

agent produced a highly alkaline solution, which was not always desirable. Furthermore, it reacted with metallic activators. Ammonium sulfide was accordingly used for sulfidizing. Unless the operations of sulfidization, activation, and coating of the particles with collector agent have been complete, the effects suffered while awaiting further treatment may be harmful. Furthermore, continuous plant operation is likely to produce better results.

Fuel-oil emulsions did not give good floats. Large amounts of xanthates proved necessary. Extractions of 80 percent of the cobalt and 67 percent of the copper were realized. Cu minerals floated with the Co minerals.

224. DEAN, R. S. Flotation of Nonsulfide Minerals, Stainerite. Bureau of Mines Rept. of Investigations 3306, 1936, pp. 20-21.

"The mineral stainerite, which contains most of the Co in an ore from Nevada, has been studied recently, and some work has been done on the use of sodium hydrosulfite in its separation by flotation. An effort to find a cheaper reagent for the flotation of a cobalt ore from Goodsprings, Nev., consumed some time, but met with little success. Aged and impure sodium hypophosphite was used in hot pulps, but the recovery of cobalt was low. Fresh hypophosphite may be as effective as the hydrosulfite since it is as powerful a reducer and is more desirable because it is relatively cheap.

"Some extraction tests were made on black cobalt oxide and clean stainerite with aqueous solutions of ammonium hydrosulfide and sodium hydrosulfite. Both the hydrosulfide and hydrosulfite exerted a sulfidizing action on cobalt oxides. The hydrosulfite probably reduces the Co₂O₃ to the cobaltous state, and the alkali sulfide causes formation of cobaltous sulfide which enhances flotation. Later the homemade Aviol 100 emulsion, used to the extent of 2 lb. per ton of ore (0.2 lb. Aviol 100 per ton), gave a high-grade stainerite concentrate with high recovery. Two pounds of ammonium sulfide were used to condition the ore and a small amount of sodium silicate to depress the calcite. The emulsion is a much cheaper reagent than the sodium hyposulfite used earlier in the investigation."

225. ———. Flotation of Cobalt Ores and Metal Recovery. Bureau of Mines Rept. of Investigations 3547, 1941, p. 36.

"Cobalt is one of the less common metals, and although not on the list of strategic metals, it is one that is not produced from domestic sources in large enough quantity to supply the domestic demand. Cobalt occurs in the Goodsprings, Nev., district. Ore-dressing tests of these ores have been carried out by the Ore-Dressing Section of the Bureau (of Mines), and resulted in a flotation procedure to produce a bulk concentrate containing Co and Cu. The Electrometallurgical Section has undertaken some work on the separation of Cu and Co from the Goodsprings ores.

"The minerals are stainerite, malachite, dolomite, some quartz, and iron oxides. Further ore-dressing tests along the lines of differential flotation were made, with indications of ultimate success. However, a good ore-dressing result, as such, would not produce a product free enough from Cu to meet all specifications for cobalt oxides. Consequently, other methods are being tested. Good evidence has been obtained that Co can be leached from the bulk-flotation concentrates and economically recovered by electrolysis. This investigation was begun only recently, and results will be published when conclusive data are obtained."

223. GLAZKOVSKII, V. A. (Inst. Mekhanicheskoi Obrabotki Poleznukh Iskopaemikh Mekhanobr (Inst. Mech. Treatment Ores). [Investigating and Concentrating Iron-Chromium-Nickel Ores of the Malinskii Deposit and of Manganese Ores of the

Labinskii Deposit in Northern Caucasus.] Concentration and Agglomeration of Iron Ores in U. S. S. R., 1932, pp. 170-184; Chem. Abs., vol. 28, 1934, p. 3350¹.

The Malkinskii deposit consists of magnetite, hematite, and brown bog iron ore, and contains Ni 0.20-0.55 percent, Co 0.06-0.14 percent, with large percentages of Fe₂O₃ and SiO₂. Flotation and magnetic separation produced Fe concentrates, leaving Ni in the tailings product.

227. KECK, W. E. Froth Flotation for Reclaiming Minerals. *The Frontier*, vol. 5, No. 1, 1942, pp. 10-12; Chem. Abs., vol. 36, 1942, p. 2821⁴.

Describes the froth flotation of amygdaloidal Cu "sands" of the Cu country of Michigan by mahogany sulfonates. Commercial plant tests show that this method is applicable also to another sand accumulation and a refractory Cu ore of the district. The sulfonates are of value in the flotation of the oxidized ores of Pb. A process consisting of a combination of gravity concentration and flotation is in commercial operation on a sludge made by grinding of a cutting alloy composed of Cr, Co, and W.

228. McLAREN, D. C. Mining Cobalt Ore at Silanco. *Canadian Min. Jour.*, vol. 66, 1945, pp. 141-145; Chem. Abs., vol. 39, 1945, p. 1829⁵.

Outlines the beneficiation of a complex Co ore in the Co area of Ontario and presents a flowsheet.

229. PECORA, W. T. Nickel Silicate and Associated Nickel-Cobalt-Manganese Oxide Deposits Near São Jose do Tocantins, Golaz, Brazil. *Geol. Survey Bull.* 935-E, 1944, p. 658.

Measured tonnage reserves of ore at 2-percent Ni-cutoff grade are 184,000 metric tons, mostly of 4-percent Ni ore. Indicated tonnage reserve is much higher, with inferred maximum reserve 9-16 million tons averaging 1-3 percent Ni. There are 20,000-75,000 tons of black concretionary pebbles, expected to contain 1-2 percent Co, which can be recovered by screening.

Leonardos reports that the German firm of Krüff, Groppe, and Humboldt experimented with nickel silicate ores from Golaz averaging 4.4 percent Ni and that in these tests they produced by flotation a concentrate containing 10 percent Ni, with an 80-percent recovery.

230. RUNKE, S. M., AND O'MEARA, R. G. Beneficiation of Arkansas Bauxite. *AIME Tech. Pub.* 1698, 1944, 9 pp.; Chem. Abs., vol. 38, 1944, p. 5175⁵.

In investigating ore-dressing methods for Al beneficiation, it was found that, by tabling a ground product, a concentrate assaying 4.93 percent Ni and 2.29 percent Co could be obtained.

231. SHAKHOV, G. A. [Flotation of Oxidized Nickel Ore.] *Russian Patent* 54,155, Nov. 30, 1938; Chem. Abs., vol. 35, 1941, p. 1369⁶.

The ore is preliminarily roasted in an atmosphere of SO₂ or in a mixture of sulfur-containing substances with the addition of coal and a base, for example, lime, to obtain slintered sulfides of Ni or Fe, and then subjected to flotation to concentrate the Ni-bearing minerals.

232. ZAPFFE, C. A. Iron Ores of the Cle Elum District, Washington. *Washington State Dept. Conservation Development, Div. Mines, Rept. of Investigations* 5, 1944, 27 pp.; Chem. Abs., vol. 38, 1944, p. 1983⁷.

The deposits are lateritic ores formed by the alteration of saxonite. Average analyses are given. The principal minerals present are magnetite, goethite, hercynite, diaspore, and fayalite, with appreciable amounts of garnierite and chromite. Beneficiation is not practicable, and the high Al, Ni, and Cr contents cause metallurgical complications. Estimates of ore reserves are given.

ORE DRESSING; NONOXIDIZED ORES

233. ALLEN, C. F., AND KENTRO, D. M. (assigned to American Cyanamid Co.). Treatment of Ores Containing Cobalt and Nickel. *U. S. Patent* 2,399,845, May 7, 1946; Chem. Abs., vol. 40, 1946, p. 4337¹.

Improvements in beneficiating cobalt and nickel sulfide ores by froth flotation, using selective depressants for the pyrite and/or marcasite, are described. The preliminary Cu-Pb float, at pH approximately 9 to 10, leaves the Co-Ni minerals which are treated with an alkali ferro- or ferri-cyanide, and an oxidizing agent, such as alkali dichromates or permanganates, to give a flotation concentrate containing Co 5 to 11 and Ni 6.5 to 16 percent.

234. AMDAHL, T. [Nickel Mines at Hösanger, Norway.] *Tidsskr. Kjem. og Bergvesen*, vol. 18, 1938, pp. 76-80; Chem. Abs., vol. 33, 1939, p. 3300⁴.

The Ni occurs as Ni magnetite with pentlandite, magnetite, Cu blende, and pyrites, the ore containing approximately 6 percent Ni and 2 percent Cu. It lies on biotite-margarite gneiss and undergoes a gradual transition upward into scapolite-containing gabbro. The winning, crushing, and flotation processes are described.

235. ANDERSON, A. K., AND HALFORD, D. S. The Concentration of the Cobalt Ores of the Agaunico Cobalt Mines, Ltd., Cobalt, Ontario. *Canadian Dept. Mines, Mines Branch Rept.* 724, 1932, pp. 80-90; Chem. Abs., vol. 26, 1932, p. 4778.

An ore of cobaltite, smaltite, and erythrite in a diabase gangue with small amounts of calcite assaying Co 2.60 and Ni 0.60 percent, Ag 0.22 and Au 0.02 oz. per ton was treated by flotation. By using soda ash 7.0 and Flotagen 0.05 lb. per ton in the ball mill and Flotagen 0.10, pine oil 0.25, and CuSO₄ 1.0 lb. per ton in the flotation machine, a concentrate (11.93 percent) assaying 17.76 percent Co and containing 83.67 percent of the Co, a middling (10.16 percent) of 1.54 percent Co containing 16.18 percent more of the Co and a tailing (77.91 percent) assaying 0.33 percent Co were obtained. Flotation tests were made on samples from various parts of the present gravity-separation plant with varying degrees of success.

236. BENENSON, V. D. [Selective Flotation of Complex Ores.] *Tsvetnye Metal*, vol. 20, No. 4, 1947, pp. 7-11; Chem. Abs., vol. 43, 1949, p. 1693d.

Cu, S, Co, Au, and Ag are extracted from the ore. Cu and Co together are removed from the ore by collective flotation, carried out at pH 8-8.2 with butyl xanthate 80-100 and flotation oil 50-60 gm./ton. Later, Cu and Co are separated by selective flotation.

237. BOSQUI, F. L. The Separation of Cobalt and Copper Minerals by Selective Flotation. *South African Min. Eng. Jour.*, vol. 46, 1936, Pt. II, pp. 661-662; Chem. Abs., vol. 30, 1936, p. 4127¹.

About 75 percent of the Co occurring as carrollite (CuCo₂S₄) at Nkana is recovered in the flotation of the Cu. In a reverberatory it remains in the matte, but in the converter the Co is found in the slag, which is granulated and worked up to an electric furnace alloy, assaying 55 percent Co.

The bulk Cu and Co concentrates after filtration are repulped and floated in a cyanide circuit to produce a Cu concentrate, with the tailing carrying most of the Co. The tailing is reground and refloatated in a fresh-water circuit to give a concentrate with Cu 47 and Co 4.35 percent. The tails are recycled.

238. CUNNINGHAM, J. R. (assigned to California Research Corp.). Flotation Separation of Cobalt. *U. S. Patent* 2,403,640, July 9, 1946; Chem. Abs., vol. 40, 1946, p. 5004¹.

In a mixture of cobaltite with chalcopyrite, pyrite,

pyrrhotite, and siliceous gangue, it is possible to make a clean concentrate of the Co by selective flotation. The pulp (20-30 percent solids) is made alkaline with lime and the chalcopyrite floated with pine oil and potassium ethyl xanthate. The tailing is acidified with sulfuric acid to pH 4-7, and a bulk concentrate of the remaining sulfides removed, the gangue is rejected at this point. The sulfide concentrate is then treated with additional pine oil and xanthate, together with a depressor for cobaltite (for example, monocalcium aryl sulfonate), and an activator such as ferric sulfate, and the pyrite and pyrrhotite are floated away from the cobaltite.

239. DURHAM, L. P. Nkana Mine Concentrator. *Trans. AIME*, vol. 112, 1934, pp. 925-934 (*see Chem. Abs.*, vol. 24, 1930, p. 3972.); *Chem. Abs.*, vol. 29, 1935, p. 7239³.

The ore consists of more or less silicified shale containing disseminated bornite, chalcopyrite, chalcocite, carrollite, and covellite. The flowsheet for the concentrator is given and discussed. The mill feed assays Cu 4.34, Fe 2.78, S 1.79, Co 0.22, and SiO₂ 44.88 percent; the flotation concentrates assay Cu 53.94 (recovery 88 percent), Fe 9.58, S 23.07, Co 2.13 (recovery 69.6 percent), and SiO₂ 5.86 percent; the tailings assay Cu 0.56, Fe 2.15, S 0.16, Co 0.072, and SiO₂ 47.86 percent.

240. EAST, J. H., JR., TRAVERS, W. M., JR., SANFORD, R. S., AND WRIGHT, W. S. Yakobi Island Nickel Deposit, Sitka Mining District, Alaska. Bureau of Mines Rept. of Investigations 4182, 1948, pp. 26-28, 28 pp.; *Chem. Abs.*, vol. 44, 1950, p. 3850h; *British Abs.*, 1948, p. A-1-161.

The location, accessibility, topography, history, and geology of the deposit are detailed. The ore consists of pyrrhotite, pentlandite, chalcopyrite, and magnetite, occurring in norite. All of the Ni and Cu occurs in irregular sulfur-bearing zones. A representative sample assays 0.34 percent Ni. Beneficiation tests show two satisfactory procedures: bulk flotation recovers 70 percent of the Ni and 85 percent of the Cu in a concentrate containing 4.8 percent Ni and 3.5 percent Cu, which after smelting gives a Ni-Cu matte; a more complex differential flotation gives 78-percent recovery of Cu in a concentrate of 20 percent and 68-percent recovery of Ni in a concentrate assaying 7.4 percent Ni.

241. FINE, M. M., BROWN, W. E., VAHRENKAMP, G. J., AND KNICKERBOCKER, R. G. (Bureau of Mines, Rolla, Mo.). Concentration of the Complex Copper-Lead-Nickel-Cobalt Ores of Southeast Missouri. *Trans. AIME*, Tech. Pub. 3099B (in *Min. Eng.*, vol. 3, No. 7, 1951, pp. 602-604); *Chem. Abs.*, vol. 45, 1951, p. 7931c; *Metals Rev.*, vol. 24, No. 8, Aug. 1951, p. 19 (187-B).

The source of most of the Co and Ni is siegenite (Co, Ni)₂S₄, a member of the linnaeite series. A test run on a composite from 15 tons showed that separate concentrates of Pb, Cu, and Co-Ni could be produced by grinding and flotation on a laboratory and pilot-plant scale. An industrial plant built subsequently produced such concentrates during the war years. Present commercial production is limited to Pb and Cu concentrates, but research is continuing to permit economic utilization of the Ni and Co values.

242. GODARD, J. S. Experimental Flotation Tests on Cobalt Ores From the Yorkshire Cobalt Mines, Ltd., Cobalt, Ontario. Canadian Dept. Mines, Mines Branch Rept. 724, 1932, pp. 160-163.

Cobaltite occurs in fine crystals in a diabase gangue assaying (2 lots) Co 2.19, 2.70; Ni 0.04, 0.03; As 2.85, 3.55 percent, and Ag 1.18, 0.46 oz. per ton. Flotation gave Co recoveries of 78 and 83 percent. The ore is slow to respond to flotation. Tabling of the tailings gives a low-grade product.

243. ———. Flotation Tests on a Sample of High-Grade Cobalt Ore From Kenora Prospectors and Miners, Ltd., Toronto, Ontario. Canadian Dept. Mines, Mines Branch Rept. 728, 1932, pp. 75-76; *Chem. Abs.*, vol. 27, 1933, p. 3173.

An ore containing 15.81 percent Co with pyrite and Zn blende was floated to give 97-percent cobalt recovery in a concentrate carrying 24.77 percent Co. A 29.5-percent concentrate was obtained at 85-percent recovery.

244. HOLT, S. P., AND MOSS, J. M. Exploration of a Nickel-Copper-Cobalt Deposit at Funtier Bay, Admiralty Island, Alaska. Bureau of Mines Rept. of Investigations 3950, 1946, 15 pp.; *Chem. Abs.*, vol. 41, 1947, p. 4071f.

An ore containing Ni 0.26, Cu 0.30, Co 0.07, Pb less than 0.05, As less than 0.01, Fe 10.6, S 0.6, and SiO₂ 36.7 percent was tested by magnetic separation, bulk flotation, and selective flotation. Magnetic separation does not concentrate Cu or Ni to any great extent. Bulk flotation does not concentrate Cu appreciably, but does concentrate Ni. By selective flotation, 79.8 percent of the Cu can be recovered in an 18.4-percent concentrate and 66.5 percent of the Ni can be recovered in a 3.59-percent concentrate.

245. HUNDHAUSEN, R. J. Investigation of Shamrock Copper-Nickel Mine, Jackson County, Oreg. Bureau of Mines Rept. of Investigations 4895, 1952, 12 pp.; *Chem. Abs.*, vol. 46, 1952, p. 9038h.

Describes the mineralization. Pyrrhotite, pentlandite, and chalcopyrite occur as disseminations, blebs, veinlets, and masses in norite. A 200-pound batch of representative ore was tested assaying 1-3 percent Ni. Fine-flake graphite interfered with flotation treatment. Because of the intimate association of sulfide minerals, the ore was not amenable to any ore-dressing methods tried for the production of separate high-grade concentrates of Ni and Cu.

246. INTERNATIONAL NICKEL CO. Operation of the Creighton Mill and 13th Shaft. Canadian Min. Met. Bull., vol. 45, No. 481, May 1952, pp. 253-259; *Trans. Canadian Inst. Min. Met.*, vol. 55, 1952, pp. 163-169; *Min. World*, vol. 13, November 1951, pp. 38-39; *Min. Mag.*, vol. 85, October 1951, pp. 210-211; *Eng. Index*, 1952, p. 676; *Metals Rev.*, vol. 25, No. 7, July 1952, p. 25 (210B), and vol. 25, No. 1, January 1952, p. 20 (6B) (4B).

The International Nickel Co. of Canada schedules mining operations for completion by 1953, with increased hoisting capacity from 5 underground mines to 13 million tons of ore per year. Describes the underground crushing, ore conveying, dust control, grinding, flotation, reagent handling, operation of sand fill plant, tailings disposal, concentrate pumping, sampling, and assaying.

247. LUTJEN, G. P. Cobalt at Fredericktown, Mo. *Eng. and Min. Jour.*, vol. 154, No. 12, Dec. 1953, pp. 72-76. *Eng. Index*, 1954, p. 206.

Describes mining and milling operations at Fredericktown, Mo. The new installation is designed to produce 1,400,000 lb. of cobalt annually, using feed containing 2.5-2.75 percent Pb, 0.5-0.75 percent Cu, 0.25 percent Ni and Co, and 5.6 percent Fe. Discusses ore treatment and selective flotation.

248. MACDONALD, W. T. (assigned to International Nickel Co. of Canada, Ltd.). Ore Flotation. Canadian Patent 335,613, Sept. 12, 1933; *Chem. Abs.*, vol. 27, 1933, p. 5706.

Ore containing sulfide minerals of Cu, Ni, and As is ground wet to free the minerals. Enough lime is added to the ore, preferably during the grinding stage, to make the pulp alkaline. A collecting agent, such as xanthate, is also added to the ore pulp, preferably dur-

ing the grinding stage. An alkali cyanide, zinc sulfate, and a frothing agent, such as pine oil, are mixed with the pulp, it is subjected to flotation, and a froth concentrate is obtained, containing a large proportion of the Cu present in the original ore. Substantially all of the Ni mineral in the original ore is inhibited from flotation. The remaining pulp is mixed with small quantities of copper sulfate, xanthate, and pine oil and subjected to a second flotation. The concentrate contains a large proportion of the Ni mineral present in the original ore.

249. MINING WORLD. Blackbird, Idaho, New Mine for Howe Sound. Vol. 13, No. 12, November 1951, pp. 40-43; Eng. Index, 1952, p. 196.

A report on the new mine and mill of the Calera Mining Co. The ore occurs in pod-shaped shoots. The Blackbird district is divided into two zones, with continuous mineralization between them. A cobalt concentrate will be produced by long conditioning with lime at high temperature. The tailings will be used for filling stopes.

250. MOYER, S. P. (assigned to American Cyanamid Co.). Flotation of Cobaltite. U. S. Patent 2,573,865, Nov. 6, 1951; Chem. Abs., vol. 46, 1952, p. 2764d.

Ore carrying cobaltite, chalcopryite, pyrrhotite, and pyrite with 2.7 percent Cu and 0.75 percent cobaltite was subjected to processing by flotation methods, obtaining 92.1 percent of the Cu in a rougher float product; finally 62 percent of the Co was obtained in a float concentrate.

The ore, ground with lime and sodium cyanide, was floated at pH 9 using 0.05 lb. per ton of the sodium salt of diethyldithiophosphoric acid and 0.09 lb. per ton of a frother containing 60 percent saturated paraffin alcohols and 40 percent light hydrocarbon oils. Fe was next floated with sodium ethyl xanthate, more frother, and pine oil. Finally the underflow was treated with calcium sulfate and hydrofluoric acid, and Co was floated with additional sodium ethyl xanthate and frother.

251. PARSONS, C. S., AND OTHERS. Copper-Nickel Ore, B. C. Nickel Mines, Ltd., Choate, B. C. Canadian Dept. Mines and Resources, Bureau of Mines Rept. 776, 1937, pp. 43-82; Chem. Abs., vol. 32, 1938, p. 5741¹.

The ore was slow-floating, even in acid circuit. Nickel and copper sulfides floated faster than pyrrhotite, which had to be recovered, as it contained Ni. Heavy oils as collectors produced low-grade concentrate with 92- to 96-percent recovery of Ni. Substitution of sodium silicate for soda ash and of amyl xanthate for heavy oil raised the grade to 6 percent Ni, but the recovery fell to 92 percent. Conditioning with air depressed pyrrhotite, raised the grade, and decreased recoveries. Cresylic acid was a good promoter but lacked frothing power; added frothers decreased the grade. Cupric sulfate was essential to high recoveries. Higher grade recoveries were obtained with a thin pulp. An 8-percent Ni concentrate at 90-percent recovery can be obtained in a thin pulp with cresylic acid as a promoter and a suitable frother.

252. —. Investigations in Ore Dressing and Metallurgy, July to December 1938. Canadian Dept. Mines and Resources, Mines and Geol. Branch, Bureau of Mines Rept. 797, 1940, 132 pp.; Chem. Abs., vol. 34, 1940, p. 7800².

Extraction studies on various ores combining Ni or Co with noble metals, or on flotation concentrates are reported, many in great detail.

253. PARSONS, C. S., WALKER, G. B., AND ANDERSON, A. K. The Concentration of Copper-Nickel Ore of the Falconbridge Nickel Mines, Ltd., Garson, Ontario,

Canadian Dept. Mines, Mines Branch Rept. 724, 1932, pp. 29-44; Chem. Abs., vol. 26, 1932, p. 4568.

A sulfide ore assaying Cu 1.11 percent, Ni 2.28 percent and a basic gangue was jigged, concentrated on a Butchart table, concentrated on a Plat-O table, and floated. Gravity concentration gave little improvement. Grinding with soda ash (4.0 lb. per ton of ore) and flotation of Cu with cresylic acid (0.04 lb.), followed by flotation with 0.20 lb. American Cyanamid reagent No. 404, or 0.20 lb. No. 423+0.20 lb. cresylic acid, gave recoveries of 99 percent of the Cu and 95 percent of the Ni.

254. PERRAULT, R. [Electromagnetic Enrichment of Ores.] Génie civil, vol. 109, 1936, pp. 356-358; Chem. Abs., vol. 31, 1937, p. 3427².

This method can be used on ores only slightly magnetic, such as Cr or Mn ores, hematite, or Fe₂O₃. New improvements in calcining at low temperatures may permit utilization of ores low in Fe. Recent applications include changing hematite to a very magnetic sesquioxide or to Fe₂O₃, and changing arsenious ore of Co and Ni to the magnetic oxides. Arsenic sulfide ores of Cu containing precious metals are ground and heated with iron oxides at 600° C. for 9 hr., and the constituents separated by consecutive magnetic treatment. This yields 97 percent of the Cu, 89.5 percent of the Au and 92.8 percent of the Ag. The Algerian mixture of blende, galena, and chalcopryite is first separated by gravity, then calcined at 525° C. for 15 min., rapidly cooled, and separated further by an electromagnet.

255. PRISTOUPIL, V. [Nickel-Copper Ore of Šluknov.] Chem. Obzor, vol. 11, 1936, pp. 42-46, (in English, 46); Chem. Abs., vol. 30, 1936, p. 6679¹.

The Ni-Cu ores of Šluknov, belonging to a normal type of Ni pyrrhotites and deposited in the proterobase, can be floated and treated by hydrometallurgical, pyrometallurgical methods on a laboratory scale.

256. REED, G. C., AND HERDLICK, J. A. Flotation of Ores From Blackbird Cobalt Deposits, Lemhi County, Idaho. Bureau of Mines Rept. of Investigations 4012, 1947, 14 pp.; Chem. Abs., vol. 41, 1947, p. 4067e.

A high recovery of metal can be made by bulk flotation of ore containing Co 0.4-1.0 and Cu 2 percent. Selective flotation of an ore containing Co 0.39 and Cu 1.35 percent gave a Co concentrate assaying Cu 10.7 and Cu 1.0 and a Cu concentrate assaying Cu 26.8 and Co 0.5 percent. As Fe sulfides increase, recovery decreases because of the difficulty of separating them from cobaltite. From an ore containing Co 3.35, As 5.2, Cu 0.45, Fe 8.1, and insoluble 60.4 percent, a Co concentrate was made that assayed Co 26.2, As 36.9, Cu 0.96, Fe 5.2, and insoluble 8.0 percent at 91-percent Co recovery.

257. ROY, R. N. Copper-Nickel Deposits of the Stillwater Complex, Stillwater and Sweetgrass Counties, Mont. Bureau of Mines Rept. of Investigations 4431, 1949, 10 pp.; British Abs., 1950, p. B-1-429.

The ore at the Mount mine comprises pyrrhotite, chalcopryite, and pentlandite with a little pyrite in irregular pods and lenses in hornfels and norite between granite and basic igneous rocks, mainly olivine and pyroxene. Mineralized core samples from 8 diamond-drill holes contained Cu 1.3 percent maximum, 0.37 percent average, and Ni 1.35 percent maximum, 0.42 percent average. A large composite sample containing Ni 0.75, Cu 1.28, Fe 35.0, and S 20.3 percent crushed to -200-mesh and floated in an acid pulp, gave a concentrate assaying Cu 8.8, Ni 2.8, and Fe 47.1 percent with Cu and Ni recoveries of 86.1 and 53.4 percent, respectively.

258. SAKSELA, MARITI, AND HACKZELL, E. [Studies on the Nivala Ores and Their Concentration.] Suomen Kemistilehti, vol. 11A, 1938, pp. 73-79 (in German,

p. 79), Chem. Abs., vol. 32, 1938, p. 8999⁷; British Chem. Abs., 1939, p. B-52.

The main minerals of Nivala ore are magnetic pyrites, pentlandite, and copper pyrites with small amounts of iron pyrites and magnetite. Cubanite and zinc blende are rarely found. The nonmetallic fraction includes olivine, serpentine, monoclinic amphibolite, chlorite, and biotite. The ore for experimentation contained 0.78 percent Ni, 0.22 percent Cu, and 9.25 percent S. Concentration of 100 gm. of ground ore at pH 5.5-6.0 by froth flotation gave 7.5 gm. of product containing 4.74 percent Ni, 1.79 percent Cu, and 27.80 percent S. A second concentration yielded 10.3 gm. containing 3.76 percent Ni, 0.62 percent Cu, and 23.60 percent S, for a total of 17.8 gm. containing 4.17 percent Ni and 1.19 percent Cu, with total recoveries of 95.2 percent of the Ni and 96.2 percent of the contained Cu.

259. SALZMANN, G. [Plant Experiences With the Flotation of Arsenical Cobalt-Nickel Ores and Bismuth Oxide Ores.] *Erzbergbau und Metallhüttenwesen*, vol. 4, June 1951, pp. 222-225; *Metals Rev.*, vol. 24, No. 8, Aug. 1951, p. 19 (193-B); Chem. Abs., vol. 45, 1951, p. 7489f.

Plant results show that these ores can be successfully beneficiated.

260. SOUTH AFRICAN MINING AND ENGINEERING JOURNAL. Production of Cobalt—Process Adopted at Nkana Mine. Vol. 54, Pt. 1, No. 2635, July 31, 1943, pp. 465, 467, and 468; Eng. Index, 1943, p. 255.

The main sources of Co are in Africa and Canada. In Northern Rhodesia, Co occurs associated with Cu in Cu mines, the principal mineral being carrollite. In the ore treated at the Nkana plant the average Co content is 0.15 percent. A flotation procedure is used, producing 2 concentrates, 1 high in Co and low in Cu and the other low in Co but high in Cu.

261. STOLZE, FRIEDRICH. [Flotation of Low-Grade German Nickel- and Copper-Bearing Ores.] *Metall u. Erz*, vol. 39, 1942, pp. 327-330; Chem. Abs., vol. 37, 1943, p. 6219⁴.

262. WALKER, G. B. Flotation Tests on Ore Sample From Denison Copper Mines, Ltd., Worthington, Ontario. Canadian Dept. of Mines, Mines Branch Rept. 724, 1932, pp. 50-54; Chem. Abs., vol. 26, 1932, p. 4777.

A chalcopyrite-pyrrhotite-norite ore assaying Cu 1.27, Ni 1.15, and S 5.73 percent was treated by flotation. In a circuit made alkaline with soda ash, a bulk Cu-Ni concentrate can be obtained with cresylic acid. High Cu recovery is indicated. The addition of 0.10 lb. per ton of Aerofloat No. 25 increases Cu and Ni recovery in a lower grade product. For the flotation of a Ni-Fe product, a water-soluble promoting agent must be used. In a CaO circuit Cu concentrate of much higher grade can be produced. The use of cyanide in conjunction with CaO has resulted in the most marked separation obtained. After the Ni-bearing pyrrhotite has been depressed by CaO and cyanide, it is most difficult to float.

263. ———. Concentration Tests on Ore Sample From Sudbury Offsets, Ltd., Levack, Ontario. Canadian Dept. of Mines, Mines Branch Rept. 724, 1932, pp. 122-129; Chem. Abs., vol. 26, 1932, p. 5044.

Chalcopyrite and pyrrhotite in norite assaying Cu 0.78, Ni 2.43, S 26.10, and Fe 24.21 percent were concentrated by various methods. Tabling followed by flotation gave no marked improvement. Flotation followed by tabling gave high recoveries of values in low-grade concentrates. Flotation in a circuit made alkaline with soda ash did not produce high-grade concentrates. Cyanide partly depressed Ni and tended to retard Cu flotation if excessive amounts were used.

Ni-Fe flotation could be effected by the use of Na₂S, CuSO₄, or H₂SO₄. A powerful promoting agent such as potassium xanthate must be used.

264. WELLS, H. R., SANDELL, W. G., SNEDDEN, H. D., and MITCHELL, T. F. Concentration of Copper-Cobalt Ores From the Blackbird District, Lemhi County, Idaho. Bureau of Mines Rept. of Investigations 4279, May 1948.

The present report gives the results of laboratory and pilot-plant studies at the Bureau of Mines Salt Lake Station. The low-sulfide ores were found amenable to selective flotation for the recovery of separate Cu and Co concentrates. In the case of ores of low Co content, flotation was supplemented by tabling of the Co flotation concentrate. In general, over 90 percent of the Cu and 75-85 percent of the Co were recovered.

The semioxidized ore was not readily amenable to beneficiation by ore dressing. Bulk flotation and subsequent refloatation for the separation of Cu and Co proved to be the most effective method. A low-grade (8.7 percent Cu) Cu concentrate was made containing 82 percent of the total Cu, and 64 percent of the Co was recovered at 8.6-percent-Co grade from a head sample assaying 1.8 percent Cu and 0.45 percent Co.

265. ZEMMEL, V. [Analysis of Copper-Nickel Ore Sample From "Noril'sk II" Deposit.] *Sovetskaya Zolotopromyshlennost*, No. 3-4, 1933, pp. 27-29; Chem. Abs., vol. 28, 1934, p. 4339⁵.

From an ore containing Cu 0.68, Ni 0.39, and Co 0.008 percent and with the Cu present as CuO 0.006, CuS 0.173, and CuFeS₂ 1.617 percent and the Ni as NiO 0.089 and NiFeS 0.814 percent, flotation gave a Cu extraction of 97-98 percent and a Ni extraction of 85 percent. The low yield of Ni is due to the fact that 18 percent of it is in the oxide form.

266. ZIMMERLEY, S. R., and RAVITZ, S. F. (Bureau of Mines, Salt Lake City, Utah). Pilot-Plant Investigation of Concentration of Blackbird Cobalt Ore by the Roast-Flotation Process. *Trans. AIME*, vol. 187, Tech. Pub. 2929B (in *Min. Eng.*, vol. 187, pp. 1044-1046); Chem. Abs., vol. 44, 1950, p. 10625i.

The ore has a high content of pyrite and some pyrrhotite and contains 0.5-1.0 percent Co and 1-2 percent Cu, which are present as cobaltite and chalcopyrite. The Cu can be recovered readily as a high-grade concentrate by selective flotation. The Co can be recovered as a bulk sulfide concentrate assaying 4-5 percent Co. It is roasted to form an oxide coating on the Fe mineral particles, and the calcine is then treated by flotation. The oxide coating prevents the Fe minerals from floating so that it is possible to obtain a high recovery of Co in concentrates assaying more than 20 percent Co. Optimum roasting temperature is 425°-450° C.

ORE DRESSING; METALLURGICAL PRODUCTS

267. BARTHEL, J. [Copper-Nickel Separation, an Example of the Application of Mineral-Dressing Techniques in Nonferrous Metallurgy.] *Freiberg, Forsch. B-6, Metallhüttenw.*, 1954, pp. 116-125; Chem. Abs., vol. 49, 1955, p. 8060h.

The processes commercially used to separate Cu and Ni are reviewed. The process involving differential flotation (*see* Chem. Abs., vol. 41, 1947, p. 4900a) is discussed in relation to the phase diagram Cu-Ni-S. The factors influencing the grain size of the phases present in a matte containing Ni 36.8, Cu 32.6, S 21.3, and Fe 3.6 percent were investigated. Thus, when the cooling rate, within the range 1.020°-500° C., was reduced from 37° C. per minute to 1.5° C. per minute, the average grain size increased from 117 to 190 microns. The examination of isothermally heat-treated specimens

showed that grain growth was predominant within the range 700°–800° C. With a cooling rate of 10° C. per hour over this interval a mean grain size of 210 microns was obtained.

- 268. HILLS, R. C.** Magnetic Separation and Settling for Nickeliferous Serpentine Ores. U. S. Patent 2,400,461, May 14, 1946; British Abs., 1950, p. B-1-289; Chem. Abs., vol. 40, 1946, p. 4650.

A 2:1 mixture of Ni-containing lateritic limonite and serpentine ore is dried, crushed to 100-mesh, preheated gradually (to avoid agglomeration) to about 540° C., and then treated with a mixture of reducing gas (to reduce the Ni to metal and the Fe₂O₃ to Fe₃O₄) and heating gas (to raise the temperature slowly to about 700°–755° C.). After 1 to 2 hr., the charge is cooled in reducing gas and leached with aeration in an aqueous solution containing 6 percent of NH₃, half of which is present as (NH₄)₂CO₃, until the leach liquor contains 1 percent of Ni. The unfiltered pulp is passed between the poles of an electromagnet or through a magnetizing coil, and then through thickeners wherein the magnetized particles agglomerate and occlude the nonmagnetic particles of the serpentine ore, causing it to settle out in the form of clusters.

- 269. INTERNATIONAL NICKEL CO.** Separation of Nickel Sulfide From Copper Sulfide (In Bessemer Mattes). British Patent 602,028, May 19, 1948; Chem. Abs., vol. 42, 1948, p. 7700f.

The cooled matte contained particles of copper sulfide, nickel sulfide, and a Cu–Ni alloy. After grinding to a fine size, a flotation process was used for separation, using the ratio of 1 pulp to 3 liquid, at a pH of about 12.4, with an addition of lime and 0.5 lb. diphenylguanidine per ton. The copper sulfide formed a rougher concentrate in selective flotation and floated in the froth. The nickel sulfide was depressed. By using several repeats, fairly good concentrates of Ni and Cu were obtained. The dewatered, re-cleaned Cu concentrate was also separated magnetically into a Ni–Cu alloy and a Ni concentrate.

- 270. LÖHN, HANS.** (Bergakad Freiberg, Germany). [Milling of Copper-Nickel Mattes.] Freiberg. Forsch. B6 Metallhüttenw., 1954, pp. 126–133 (*see* Abs. 269 and Chem. Abs., vol. 49, 1955, p. 8060h); Chem. Abs., vol. 49, 1955, p. 8061a.

Milling tests to concentrate the Ni and Cu portions of a matte containing Ni 22.72, Cu 57.10, S 18.15, and As 0.43 percent include grinding, elutriation, and flotation. The Ni concentrate contains Ni 54.4 and Cu 17.3 percent; the Cu concentrate Cu 71.0 and Ni 6.5 percent.

- 271. SCHLECHT, HELMUT, AND SCHLECHT, LEO.** [Separation of Nickel and Copper in a Copper-Nickel Matte.] Erzbergbau. u. Metallhüttenw., vol. 4, 1951, pp. 1–3; Chem. Abs., vol. 45, 1951, p. 3307b; Metals Rev., vol. 24, No. 5, May 1951, p. 19 (113-B).

Several different methods are reviewed, and also a new process. The Ni–Cu matte is thermally refined, then finely ground, and finally subjected to some mechanical separation, such as flotation, in which the Cu-bearing particles are separated from the Ni-bearing fraction of the matte.

- 272. SPROULE, W. K., AND HARCOURT, G. A.** (assigned to International Nickel Co.). Physical Method of Separating Copper and Nickel Sulfides. U. S. Patent 2,419,973, May 6, 1947; Chem. Abs., vol. 41, 1947, p. 4900a.

The method consists in cooling a molten mass of Cu–Ni Bessemer matte in a controlled manner to cause crystallization into a Cu-phase and Ni-phase, both relatively pure. The range of regulated slow cooling starts when the primary crystals of Cu₂S appear and

continues through the temperature range in which beta-Ni₃S₂ is converted into alpha-Ni₃S₂ (1,300°–950° F.). Slow cooling through this range favors diffusion of the Cu₂S crystals already present. It is preferable to continue slow cooling to about 200° F. The objective is to obtain primary crystals of 0.003–0.1 inch in size. A mass of this crystal size, when ground to 325-mesh (10–35 percent on 325 m.), is free enough of mechanical locking to enable a separation to be made in which the Cu portion contains less than 1 percent Ni, and the Ni portion less than 1 percent Cu. The separation may be effected by flotation, by electronic sorting, by magnetic separation, by sink-and-float, by solution of one component in a nonsolvent for the other, etc. The method is applicable to mattes ranging widely in composition, but the preferred range is S 20–24, Cu 15–50, and Ni 61–30 percent. The process is intended for mattes from Sudbury ores but may be used on scrap by adding S and making a synthetic matte.

- 273. SPROULE, W. K., HARCOURT, G. A., AND ROSE, E. H.** (assigned to International Nickel Co., Inc.). Froth Flotation of a Nickel-Copper Sulfide Matte. U. S. Patent 2,432,456, Dec. 9, 1947; Chem. Abs., vol. 42, 1948, p. 1866e.

Diphenylguanidine and diorthotolylguanidine are effective froth flotation agents for the separation of copper sulfide and nickel sulfide from mattes containing nickel sulfide, copper sulfide, and metallic Ni–Cu alloy. About 0.25–1.0 lb. of reagent is used per ton of matte.

CONDITIONING, SINTERING, ETC.

- 274. COMPTOIR TECHNIQUE ALBERT KNAFF ET MAYER, LEON, AND GREDT, PAUL.** [Treating Ores.] French Patent 655,296, Mar. 23, 1928; Chem. Abs., vol. 23, 1929, p. 4432.

Briquets of Mn, Cr, W, V, Mo, Ti, Ni, Co, or P ores are made by adding, with the necessary C, a lower oxide of Fe or powdered metallic Fe and an oxidizing agent. By its oxidation, the Fe or lower oxide forms an agglomerating agent and by its final reduction forms an alloy with the other metal.

- 275. GREDET, PAUL, KNAFF, ALBERT, AND MAYER, LEON.** [Briquetting Ores.] German Patent 517,735, Apr. 1, 1926; addition to German Patent 501,585 (Chem. Abs., vol. 24, 1930, p. 4752); Chem. Abs., vol. 25, 1931, p. 2677.

The method (described in German Patent 501,585) for briquetting Mn ores with C and low-stage oxidation compounds of Fe is extended to include ores of Cr, W, V, Mo, Ti, Ni, Co, and P.

- 276. METALLGESELLSCHAFT, A. G.** [Agglomerating Ores.] French Patent 745,794, May 16, 1933; Chem. Abs., vol. 27, 1933, p. 4204.

Ores that contain water of crystallization and deprecitate on heating, for example, ores of Ni containing hydrosilicates, are agglomerated by mixing them with fuel and calcining the charge in a blowing furnace while a current of air transverses it, the size of grains of the charge not being above 5 mm. and preferably below 3 mm.

- 277. MIRONOV, A. A.** [The Sintering of Ufaley Nickel Ores.] Tsvetnye Metal, 1930, pp. 48–67; Chem. Abs., vol. 27, 1933, p. 482.

Ufaley Ni ore was sintered on a Dwight-Lloyd machine. Good results are obtained when the ore is kept in contact with the flame for a longer period than usual for this machine. Anthracite breeze mixed into the ore gives better results than coke breeze.

- 278. ROACH, A. G.** Sintering at Coniston. Canadian Min. Met. Bull., vol. 248, 1932, pp. 724–742; Chem. Abs., vol. 27, 1933, p. 687.

Describes a sintering plant for treating heavy sulfide ore containing chalcopyrite, pentlandite, and nickelififerous pyrrhotite.

279. WERGELAND, O. [Sintering of Flotation Concentrate at Evje, Norway.] *Tids Kjem Bergvesen*, vol. 17, 1937, pp. 147-150; *Chem. Abs.*, vol. 32, 1938, p. 6205.

A plant for treating a concentrate containing Ni 3.7,

Cu 3.1, Fe 35, S 27, and insoluble matter 24 percent is described. The concentrate (mean particle size 75 microns) is mixed with H₂O and return product and sintered in layers 12 cm. deep in a continuous trolley belt. A reaction temperature higher than 1,200° C. is attained, yielding a product containing 3 to 6 percent of S. Gives details of layout, plant running, and dust prevention.

PART II. PYROMETALLURGICAL

PYRO TREATMENTS; GENERAL

REDUCTION TO METAL

280. BLELOCH, WILLIAM. [Theoretical Considerations in the Operation of Iron Blast Furnaces With Cold Carbon Dioxide Blast.] Jour. Chem. Met. Min. Soc., South Africa, vol. 50, 1950, pp. 255-292; Chem. Abs., vol. 44, 1950, p. 9883c.

A modified blast furnace can be built and operated at a lower cost per ton of Fe; furthermore, the furnace is smaller for a given output. A proposed blast of oxygen-enriched sulfur dioxide should produce about 300 lb. of Fe per hour per sq. ft. of hearth area compared with 180 for usual practice. Hot-blast stoves are replaced by an O_2 plant and by a plant to extract CO_2 from the furnace gases with ethanalamine. Coke ovens will be smaller. Coke can be replaced by anthracite because a cellular structure is not required for reaction with O_2 and CO_2 . Anthracite should prove to be a practical fuel for smelting the ores of Cu, Pb, Ni, Co, and the oxides of Mn, Cr, and V with carbonated blast. The use of carbonated blast should be of advantage in smelting Si-Al-Ti-bearing ores because of the ease of adjustment of hearth temperature by varying the CO_2 content of the blast.

281. BOGITCH, B. [Principles of Treatment of Nickel Ores.] Compt. rend., vol. 194, 1932, pp. 1500-1502; Chem. Abs., vol. 26, 1932, p. 4016.

The ore studied had the following composition after calcination: Ni 10.3; Fe 7.02, MgO 5.6, Al_2O_3 22.4, and SiO_2 42.5 percent. On reduction with varying amounts of C, the lower the Ni content in the slag, the greater the amount of Fe in the metal obtained. Addition of lime reduces the Ni content of the slag, while an increased Ni content is obtained when lime is replaced with $CaSO_4$. Addition of ferruginous products renders reduction of the ore more difficult.

282. BRASSERT, H. A. Reduction of Ores to Metal. British Patent 561,218, May 10, 1944; Chem. Abs., vol. 39, 1945, p. 4834⁸.

An ore containing a mixture of reducible metal compounds is subjected to the action of a reducing agent, such as C, at a temperature sufficient to reduce the most easily reducible metal. The mixture is then melted in a nonreducing atmosphere in the presence of a flux to separate the purified metal from the unreduced compounds by removing the latter as slag, which then receives the same treatment as the original ore to separate the next most easily reducible compound. When the ores contain ilmenite, lime is added to the molten mixture of Fe and unreduced material. Fe ores containing Ni and Cr are subjected to the reducing agent below 600° C.

283. BREMHORST, A. [Preparation of Metallic Cobalt From Cobaltiferous Smelter Residues.] Metall. u. Erz., vol. 24, 1927, pp. 7-8; Chem. Zentralb., 1927, p. 1518; Chem. and Ind. British Chem. Abs., vol. 46,

Oct. 14, 1927, p. 783; Bureau of Mines Inf. Circ. 6331, p. 29.

284. CLARK, W. G. (assigned to Clarkiron, Inc.). Reducing Ores Such as Those of Iron, Chromium, Nickel, Vanadium, and Titanium. U. S. Patent 2,144,618, Jan. 24, 1939; Chem. Abs., vol. 33, 1939, p. 2868¹.

A vertical furnace for reducing ores is described as consisting of a hollow, smooth bore with means for a rotating, downward ore movement, the heat supplied by induction, allowing the ore to cool in a lower sealed cooling chamber, with a port for gas introduction at the lower cooling end.

285. DOTTERWEICH, F. H. Reduction of Metallic Ores by Natural Gas. Refiner Nat. Gasoline Mfr., vol. 21, 1942, pp. 135-138; Chem. Abs., vol. 36, 1942, p. 3757⁹.

Describes the Clarkiron process for the reduction of metallic ores, in a relatively finely divided form, by natural gas. The process is available to reduce Fe, Cr, Ni, V, and Ti on a commercial basis; it promotes reduction of ores in localities heretofore ruled out by absence of coking coal and encourages development of industry where large deposits of natural gas and the desired grade of ores are available. From estimates made, this process can operate on a considerably lower dollar investment per ton of metal output than orthodox procedures.

286. DOWNIE, C. C. Nickel Blast Smelting Still Offers Advantages. Eng. and Min. Jour., vol. 147, No. 8, 1946, pp. 88-90; Chem. Abs., vol. 40, 1946, p. 6033⁸. Describes operations; accompanying flowsheet.

287. DUFFIELD, F. L. Vertical Retort Apparatus (and Mode of Working) for Reducing Iron, Copper, or Nickel Ores. British Patent 304,174, Oct. 10, 1927; Chem. Abs., vol. 23, 1929, p. 4664.

Structural features are detailed.

288. ———. Metallurgical Furnaces. British Patent 422,081, Jan. 4, 1935; divided on British Patent 422,058 (Chem. Abs., vol. 29, 1935, p. 3642⁸); Chem. Abs., vol. 29, 1935, p. 4318⁸.

An apparatus for reducing Fe, Cu, Pb, and Ni ores comprises a shallow reduction chamber provided with a heat-lagged roof which moves continuously in contact with the charge, a scraper mechanism being incorporated in the roof to convey the charge in contact with the roof and floor of the chamber.

289. EDWIN, EMIL. Metals From Oxides or Sulfides. British Patent 496,270, Nov. 24, 1938; Chem. Abs., vol. 33, 1939, p. 2867¹.

Procedure is discussed in which C, CO, and lime are heated in contact with ores to produce metals: at the elevated temperature a partial pressure of CO_2 is maintained greater than the dissociation pressure of $CaCO_3$, so that the CO_2 formed combines with CaO and the ore is reduced to metal, which may be separated magnetically on cooling. The $CaCO_3$ is calcined to CaO and recycled. Metals that may be formed in this way are Cu, Pb, Mo, W, Zn, and Ni (see Chem. Abs., vol. 32, 1938, p. 4133¹).

- 290. FOHLEN, A. H.** Combined Reduction of Ores and Hydrogenation of Carbonaceous Materials. British Patent 339,276, July 25, 1929; Chem. Abs., vol. 25, 1931, p. 2406⁶.

Ores such as those of Ni are reduced to metals, and carbonaceous materials (such as lignite and its distillation products) are hydrogenated to form volatile fuels, by first reducing the ore in the presence of carbonaceous material or its distillation products and H₂ heated to about 350°–400° C., then allowing the temperature to fall to 150°–300° C. and hydrogenating the gaseous products of the reaction by contact with freshly reduced metal. Describes an arrangement of apparatus and various details of procedure. The process may be applied to the production of hydrogenated products from anthracene, etc.

- 291. GALLO, G., AND DELGUERRA, M.** [The Reaction of Hydrogen With Metallic Oxides and Sulfides. VI]. Ann. chim. (Rome), vol. 41, 1951, pp. 51–60 (*see* Chem. Abs., vol. 31, 1937, p. 8424⁷, and Chem. Abs., vol. 23, 1929, p. 3425); Chem. Abs., vol. 45, 1951, p. 8385e.

The oxides and sulfides of a number of metals were treated with H₂, showing for cobalt oxide an initial reduction at 80° C. with a reduction to metal at 120° C.; cobalt sulfide showed an initial desulfurization at 82° C. and reduction to metal at 290° C. For nickel oxide an initial reduction is indicated at 95° C., with reduction to metal at 118° C.; nickel sulfide showed initial desulfurization at 110° C. and reduction to metal at 150° C. In general, the affinity of the metals studied is greater for S than for O, but the increase in affinity for S does not parallel the order of increase for O.

- 292. I. G. FARBENINDUSTRIE, A. G.** Reducing Metals. British Patent 321,336, Nov. 19, 1928; Chem. Abs., vol. 24, 1930, p. 2418⁵.

Compounds (such as iron chloride, nickel bromide, copper chloride, cobalt iodide, osmium oxide, and lead oxide), which are reducible by H₂, CO, powdered C, and the like but are not dissociable by heat alone, are reduced with reducing agents on the hot free space of a heated chamber.

- 293. INTERNATIONAL NICKEL CO., INC.** [Nickel.] German Patent 558,777, Apr. 27, 1930; Chem. Abs., vol. 27, 1933, p. 488.

Minerals with a high Ni content are treated in a converter with gas consisting principally of superheated steam to deoxidize and desulfurize the mineral for the production of Ni or Ni alloys. The process may be carried out in two stages: (1) At 1340°–1450° C. with steam and 10 percent air, to remove all but 2–4 percent of the S; and (2) at 1,510°–1,565° C. with steam, to remove all but 0.005–0.02 percent of the S.

- 294. JOURNAL DU FOUR ÉLECTRIQUE.** [The Electric Furnace in the Metallurgy of Cobalt.] Vol. 44, 1935, pp. 55–56; Chem. Abs., vol. 29, 1935, p. 3915⁹.

Describes electric furnaces for Co production in Africa. In Belgian Congo these are single-phase, vertical-electrode types working on charges of 6-percent Co ore mixed with slags and yielding a red and a white alloy, both of which are refined further. In Rhodesia three-phase tilting furnaces are used to smelt flotation concentrates.

- 295. KOHLMAYER, E. J.** [Combustion and Reduction of Pulverized Materials in a Countercurrent Stream of Air. With Special Application to Zinc Oxide-Coal Mixtures.] Erzbergbau u. Metallhüttenw., Berlin-Grünwald, vol. 5, 1952, pp. 385–389; Chem. Abs., vol. 47, 1953, p. 459f.

After ignition of the charge at the top, a zone of combustion extends from the top to the bottom, the upper side of which has a temperature of about 1,600° C., the

middle broad zone a temperature between 1,000° and 1,100° C., and the lower part about room temperature. As the combustion zone goes lower, the zone of constant temperature becomes broader owing to loss of moisture in the middle zone. This process was studied with materials of various particle sizes of several metal oxides, including those of Fe, Ni, and Cu. It is essential that the metal reduced move ahead of the zone of combustion.

- 296. REITLER, E.** [The Use of Greek Nickel Ores in Germany.] Metallbörse, vol. 20, 1930, pp. 2273–2274; Chem. Abs., vol. 25, 1931, p. 208².

Before the war the German Ni works used New Caledonian ore and some American oxide. Attempts have been made to use Greek Ni ores from the Laurion Mountains. The composition of these ores, on a dry basis, is: NiO 6.62, CoO 0.15, Fe₂O₃ 40.01, SiO₂ 28.86, Al₂O₃ 14.64, and As₂O₃ 0.04 percent and minor quantities of CuO, CaO, MgO, and Cr₂O₃. The smelting of these ores is complicated by the presence of so much alumina, which gives very viscous slags. It is very doubtful if these ores can be used successfully.

- 297. ROBIETTE, A. G. E.** Separation, Recovery, and Refining of Metals. British Patent 582,506, Dec. 9, 1943, and Jan. 26, 1944; British Abs., 1947, p. B-1–195.

Ni or Cu is separated from Fe, Cu from Ni or Fe, Pb from Sn and Fe, and Ni and Co from Al by blowing the molten-metal mixtures in a vertical shaft furnace with a mixture of fuel gas and gas containing O₂, so that products of combustion contain no free O₂, but H₂ and steam and/or CO₂ and CO in such proportions (for example, CO, 7–11, Co 8–1, H₂ 10–1, and H₂O 15–18 percent, balance N₂) that they are oxidizing to one metal while reducing to the other. The oxide formed is melted or slagged off, and the purified other metal is collected at the base of the furnace.

- 298. SAVELSBERG, WALTER, AND RUNTE, J.** [New Operating Practice With the Metal Blast Furnace, Especially in Smelting Nickel Ores.] Metallbörse, vol. 23, 1933, pp. 145–146, 177–178, and 209–210; Chem. Abs., vol. 27, 1933, p. 2118.

Operating details are given for a Ni blast furnace, including the fluxing necessary for matte formation and slag formation. Ores rich in Fe and low in basic oxides give low Ni yields. A systematic variation of charge gives increased yields. Contrary to general belief, MgO in the flux gives beneficial results. The heat balance of the furnace is similar to reduction-equilibrium relations in the Fe blast furnace.

- 299. SMITH, S. C.** [Nickel and Copper.] French Patent 673,119, Apr. 15, 1929; Chem. Abs., vol. 24, 1930, p. 2418.

Ores, residues, etc., containing Ni and Cu to be recovered are reduced in such a way that the metals are in sponge form; then the Ni and Cu are transformed into acid-soluble compounds by wetting with acids and exposing to the air until an elevated temperature is attained. The heat of reaction may suffice; if not, external heat is applied. Precious metals such as Pt remain undissolved.

- 300. VAN ES, A. C.** (assigned to N. V. Maatschappij Voor Zwavelzuurbereiding Voorheen G. T. Ketjen & Co.). Extracting Copper and Nickel From Their Ores. U. S. Patent 2,168,542, Aug. 8, 1939; Chem. Abs., vol. 33, 1939, p. 9272¹.

An apparatus and a process for treating oxide, silicate, or roasted sulfide ore are described. The ore is heated with a reducing gas containing steam for such a time and temperature that only the Cu and Co are reduced to metal, while Fe and metals having a higher heat of combustion than Fe are retained in the oxidized state.

ROASTING WITH A SALT OR SALT-FORMING GAS

301. ASHCROFT, E. A. Treating Ores or Concentrates of Copper, Nickel, etc. British Patent 338,556, Aug. 20, 1929; Chem. Abs., vol. 25, 1931, p. 2406².

Material containing copper or nickel sulfides or both, or Cu or Ni oxidized compounds, with added S such as in iron sulfide, is treated with air or O₂ at 600° C. to convert the Cu and Ni to sulfate (without disturbing or rabbling the materials during the reaction). The heat of reaction is usually enough to maintain the temperature after the reaction is started. The charge may be covered by a thin layer of inert material. When Ni is present, FeSO₄ or FeCl₃ may be added advantageously. Most of the Fe present remains in the residue as oxide on leaching, with sulfates of gangue materials, such as CaSO₄. Oxygen or air enriched with O₂ may be used to start or assist the reaction. Various other details and modifications of apparatus and procedure are described.

302. ———. [Copper and Nickel.] French Patent 702,549, Aug. 20, 1930; Chem. Abs., vol. 25, 1931, p. 4212².

Cu and Ni are recovered from sulfide ores or from oxides mixed with other sulfides or S compounds by the action of a stream of O₂ at 600° C. under such conditions that sulfates are obtained. FeCl₃ or FeSO₄ may be added to the materials to be treated. The Cu and Ni may be recovered by treating the sulfates with NH₃ with or without CO₂.

303. ———. [Treatment of Copper and Nickel Ores.] German Patent 598,333, July 3, 1934 (*Cl. 40a 2.50*) (*see* British Patent 338,556, Chem. Abs., vol. 25, 1931, p. 2406); Chem. Abs., vol. 28, 1934, p. 6418.

304. CLERC, H. J. M. E. [Refining Nickel and Copper.] French Patent 36,617, Mar. 30, 1929 (addition to French Patent 669,109; Chem. Abs., vol. 24, 1930, p. 1610) (*see* Chem. Abs., vol. 24, 1930, p. 815); Chem. Abs., vol. 25, 1931, p. 907².

Ni, Cu, or alloys of Ni and Cu are refined by chlorination with alkali, alkaline earth, or earth chlorides, which act to form volatile chlorides of the impurities.

305. COMSTOCK & WESTCOTT, INC. [Chlorinating Iron Ores Containing Nickel.] German Patent 633,216, July 30, 1936 (*Cl. 40a 43.01*) (*see* French Patent 775,161, Chem. Abs., vol. 29, 1935, p. 2139², and Canadian Patent 353,342, Chem. Abs., vol. 29, 1935, p. 7928²); Chem. Abs., vol. 30, 1936, p. 7531².

306. DEWAN, M. L., AND JOSHI, M. L. Cobalt Salts From Cobalt Ore. Trans. Indian Ceram. Soc., vol. 3, 1944, pp. 56-61; Chem. Abs., vol. 40, 1946, p. 4856².

The Co ore of Nepal is apparently the best available in India. It contains about 14 percent Co and no Ni. Preliminary laboratory work indicates that fusion with sodium chloride or treatment with H₂SO₄ may be used in commercial production.

307. GUERREIRO, A. [Contribution to the Metallurgy of Nickel in Brazil.] Rev. soc. brasil chim., vol. 2, 1931, pp. 493-499; Chem. Abs., vol. 26, 1932, p. 4280.

Discusses the economics and disadvantages of the former "matte" process as compared with the newly developed "Guerreiro" process.

308. HUGHES, L. M. [Chlorinating Ores.] French Patent 766,387, June 27, 1934; Chem. Abs., vol. 28, 1934, p. 7234².

Ores containing Zn, Fe, Pb, Cu, Ag, Au, Mn, Sn, Co, Ni, Cd, or V are chlorinated in at least two distinct steps. The ore is first treated with a chlorinating gas such as gaseous HCl or Cl₂, by which treatment all moisture is removed and the ore becomes porous, and then mixed with FeO and again chlorinating.

309. KUZNETSOV, A. N. [Recovery of Nickel From Ores.] Russian Patent 50,401, Jan. 31, 1937; Chem. Abs., vol. 31, 1937, p. 8491².

Nickel ore is heated with ammonium salts to a temperature not exceeding the sublimation point of the salts, and then the Ni is extracted in the usual manner.

310. LISSAUER, M., & CIE. [Separation of Metals.] French Patent 705,093, Oct. 31, 1930; Chem. Abs., vol. 25, 1931, p. 5135.

Zn, Sn, Pb, Bi, and other metals are separated from alloys of Cu or Ni by volatilization, reducing gases such as H₂, CO or water gas being introduced into the bath of fused metal, and an oxidizing atmosphere being present in the furnace. The Zn and Sn may be obtained separately by maintaining a neutral or slightly reducing atmosphere in the furnace until the Zn is eliminated. After removal of Zn, substances yielding S may be added to the bath.

311. LOSEV, K. I. [Working Up Poor Nickel Ores by Chlorination.] Tsvetnye Metal, No. 2, 1940, pp. 60-61; Khim. Referat. Zhur., No. 7, 1940, p. 74; Chem. Abs., vol. 36, 1942, p. 5447¹.

Chlorination of low-grade Ni ores is profitable only under large-scale production conditions. The consumption of Cl₂ in ores containing 1.3 percent NiO is 35.5 long tons per ton of Ni produced. FeCl₃, SiCl₄, AlCl₃, CrCl₃, and other byproducts must be recovered to make the process profitable.

312. MEYER, R. F. (assigned to Meyer Mineral Separation Co.). Recovering Metals From Their Ores. U. S. Patent 1,833,632, Nov. 24, 1932; Chem. Abs., vol. 26, 1932, p. 952.

Finely divided ore such as that of Zn, Mn, Co, Ni, or Cu is brought to a "quasiwet" condition and then treated with an acidic reagent gas such as SO₂ while continuously maintaining the "quasiwet" condition by regulated addition of moisture. Agitation is provided.

313. ——— (assigned to Meyer Mineral Separation Co.). Chloridizing Oxidized Ore Such as That Containing Nickel. U. S. Patent 1,870,863, Aug. 9, 1932; Chem. Abs., vol. 26, 1932, p. 5539.

The moistened ore is roasted with a ferrous chloridizing reagent, such as FeCl₂, at a temperature above 250° C. to form a calcine and to accumulate the chloridized metal values in the calcine, while air is introduced in smaller amount than theoretically required to oxidize the ferrous reagent to Fe₂O₃. Most of the reagent, however, is oxidized.

314. MEYER MINERAL SEPARATION Co. Treating Ores of Metals. British Patent 336,770, Sept. 30, 1929, Chem. Abs., vol. 25, 1931, p. 1789⁵.

Metalliferous material is heated in the presence of so-called "reagent metal" (defined as a metal capable of existing in two or more states of oxidation, such as Fe, Cu, Ni, or Mn) to a temperature somewhat below the decomposition temperature of the sulfate of the "reagent metal" and treated alternately with an oxidizing gas, such as air, and with an atmosphere containing SO₂ and air. The process is applicable to oxidized or sulfide ores containing Au, Ag, Pb, Ni, Mn, Cu, Co, Bi, Zn, Cd, Fe, and similar heavy metals (which may themselves contain enough "reagent metal" or may be mixed with pyrites to supply the latter). If the ore is not amenable to sulfating, a halide such as NaCl may be gradually added to form chlorides.

Gives various details and examples.

315. MOROSOV, I. S., URAZOV, G. G., AND EFREMOV, A. N. [Treating Low-Grade Copper-Nickel Ores With Chlorine.] Russian Patent 51,631, Aug. 31, 1937; Chem. Abs., vol. 33, 1939, p. 9272².

Chlorides of Ni, Cu, Fe, and Mg are produced by passing gaseous chlorine with 1 percent of SCl_2 or SCL through the ore at 500°C . After the chlorides are extracted, NaOH is added in a sufficient amount to selectively precipitate nickel hydroxide, but not $\text{Mg}(\text{OH})_2$.

316. OSTHOFF, R. C., AND WEST, R. C. Chlorination of Metals in Presence of Donor Solvent. *Jour. Am. Chem. Soc.*, vol. 76, No. 18, Sept. 20, 1954; *Eng. Index*, 1954, p. 642.

Methods are presented for low-temperature chlorination of Co, Ni, Mn, Zn, and Cr in several solvents. Relatively pure anhydrous metal halides or coordination compounds may be isolated. It is shown that the halogenation of metals in the presence of donor solvents is a rather general reaction.

317. POOLE, H. G., AND RAVITZ, S. F. (assigned to the United States of America as represented by the Secretary of the Interior). Nickel Recovery. U. S. Patent 2,520,958, Sept. 5, 1950; *Chem. Abs.*, vol. 44, 1950, p. 9910a.

The pulverized ore is mixed with an equal weight of ammonium sulfate, baked at $400^\circ\text{--}600^\circ\text{C}$. for several hours, and cooled. It is then leached with a strong ammonia, ammonium carbonate solution, and the separated liquid is evaporated to produce a hydrated nickel ammonium sulfate salt; 95-percent recovery of Ni is claimed.

318. SAVELSBERG, WALTER (assigned to Allgemeine Elektro-Metallurgische G. m. b. H.). [Separating Cobalt From Nickel.] German Patent 504,437, Dec. 28, 1928; *Chem. Abs.*, vol. 24, 1930, p. 5281.

Ores, etc., containing Co and Ni as oxides or hydroxides, are calcined with SO_2 or S at 500°C . in the presence or absence of steam, and the mixture of sulfates so obtained is heated at $1,200^\circ\text{C}$., whereby NiSO_4 is decomposed while CoSO_4 is not. The Co is then extracted with water acidified with H_2SO_4 .

319. ———. [Separating Nickel and Cobalt.] French Patent 688,491, Jan. 20, 1930 (*see* German Patent 504,437; *Chem. Abs.*, vol. 24, 1930, p. 5281); *Chem. Abs.*, vol. 25, 1931, p. 676¹.

320. STEPHENS, F. M., JR. (Battelle Memorial Inst., Columbus, Ohio). The Fluidized-Bed Sulfate Roasting of Nonferrous Metals. *Chem. Eng. Prog.*, vol. 49, 1953, pp. 455–458; *Chem. Abs.*, vol. 47, 1953, p. 11009g.

The ease with which temperatures and atmospheres can be controlled in the fluidized-bed reactor makes it ideally suited to selective sulfate roasting. The process has not been widely used because it cannot be satisfactorily controlled in other equipment. The paper describes test work that has been carried out on a pilot-plant scale and has shown that the fluidized-bed reactor can be used successfully for treating Co and Cu ores to produce water-soluble sulfates while retaining the Fe in the insoluble oxide form.

320a. SULPHIDE CORP. [Treating Ores.] French Patent 711,826, May 31, 1931; *Chem. Abs.*, vol. 32, 1938, p. 89⁸; *Chem. Abs.*, vol. 26, 1932, p. 1562.

Ores containing Fe and other metals such as Ni, Cu, Zn, or Pb are treated with Cl_2 and an inert diluent in a closed cycle to form chlorides of the metals present and to volatilize the nonferrous chlorides and at least a part of the FeCl_3 . The chlorides are condensed, and the FeCl_3 is oxidized to form iron oxide with regeneration of dilute chlorinating gases. Oxide ores are first treated to reduce the oxides to the metallic state. If sulfide ores are treated, S is also recovered from the exit gases. Ni and Co may, if desired, be recovered, with the Fe as oxide. The metals other than Fe may be freed from Fe either by forming and volatilizing

FeCl_3 or by oxidizing the FeCl_3 to Fe_2O_3 and oxide and leaching the residual mixture of chlorides from Fe_2O_3 .

321. TAFEL, V., AND LAMPE, G. [The Conversion of the Nickel Content of Various German Nickel Ores and Minerals Into Soluble Form.] *Metallwirtschaft*, vol. 16, 1937, pp. 1038–1041; *Chem. Abs.*, vol. 32, 1938, p. 89⁸.

Roasting ores and minerals from the Frankenstein district in O_2 -enriched air containing SO_2 or SO , makes a high percentage of the Ni content of the ore water-soluble. Addition of NaCl to the ore helps in some instances.

322. WATARASE, TAKEO, AND OTHERS (assigned to Gakuta Industries Co.). [Refining of Ores High in Arsenic.] Japanese Patent 57, Jan. 9, 1953; *Chem. Abs.*, vol. 48, 1954, p. 535g.

Powdered Ni ore is mixed with 5–10 percent bleaching powder, heated in a reaction tube at $300^\circ\text{--}400^\circ\text{C}$. while Cl_2 gas is passed to vaporize AsCl_3 and SbCl_3 . The residue containing NiCl_2 , FeCl_3 , CoCl_2 , CuCl_2 , PbCl_2 , etc., is dissolved in warm water, and the ingredients are separated by a wet method.

SMELTING TO FERROALLOYS

323. FRIEDRICH KRUPP GRUSONWERK, A. G. [Recovering Metals.] French Patent 781,043, May 8, 1935; *Chem. Abs.*, vol. 29, 1935, p. 5799⁸.

Metals such as Ni, Co, and Cu are recovered from their ores by reduction, sometimes adding Fe compounds, at such a temperature below the melting points that ferroalloys of these metals are formed, and which may be separated after cooling. S, As, or phosphate substances may be added to make these alloys more stable when hot.

324. ———. [Nickel Ores.] French Patent 794,756, Feb. 25, 1936; *Chem. Abs.*, vol. 30, 1936, p. 5168⁸.

The ore is subjected to a reduction in which Ni, as well as part of the Fe of the ore, is reduced. Alloys of Ni containing Fe are prepared and afterward enriched in Ni by oxidation and scorification of the Fe.

325. HORTON, F. W. Production Problems Face Ferroalloy Metallurgists. *Eng. and Min. Jour.*, vol. 145, No. 2, 1944; *Chem. Abs.*, vol. 38, 1944, p. 1451⁸.

A review for 1943 is presented. Alloying elements discussed are Ni, Co, B, Cr, Mn, Mo, and V.

326. JOHANSEN, FRIEDRICK. [Survey of the Recovery of the Most Important Steel-Alloying Metals.] *Metall u. Erz*, vol. 41, 1944, pp. 79–84; *Chem. Abs.*, vol. 39, 1945, p. 259².

With all the important steel-alloying metals, a rich metallic oxide is first obtained from the raw ore. Although this still contains gangue and iron oxide, it must be free from S, As, and P. In the second stage of the recovery, these oxides are reduced to pure metal or a ferrometal. For recovering Si, Mn, Cr, V, W, and Ti, the starting point is oxidic ore, while the greater part of Mo, Ni, and Co is obtained from sulfidic ores.

327. KALLING, B., AND LINDBLAD, A. Methods of Producing Metals and Ferroalloys Having Regard to Swedish Conditions. *Bull. Iron and Steel Inst.*, vol. 84, December 1942, p. 42a; *Eng. Index*, 1943, p. 653.

Discussed are methods for producing ferrosilicon, silicoaluminum, ferromanganese, spiegel, silicomanganese, ferrochrome, ferrotungsten, ferromolybdenum, ferrovanadium, ferrotitanium, silicocalcium, and ferrophosphorus, as well as the nonferrous metals Al, Mg, Zn, Pb, Cu, Ni, Sn, and Co, used in Sweden and Norway. A very brief extract from *Jernkontorets Annaler* vol. 125, No. 8, 1941, is given.

328. LYON, D. A., KEENEY, R. M., AND CULLEN, J. F. Ferronickel; the Electric Furnace in Metallurgical Work. Bureau of Mines Bull. 77, 1916, pp. 151-154.

Most ferronickel is produced by simply incorporating Ni or a Ni alloy in steel. In the three instances cited, however, it was made directly from the ore.

In 1907, during the course of experiments on the production of pig iron in electric furnaces at Sault Ste. Marie, Ontario, several runs were made on the reduction of roasted nickeliferous pyrrhotite with charcoal. Tables are presented showing analyses of the pyrrhotite, limestone, flux, slag produced, and the 4-percent-Ni ferronickel. The results show the possibility of producing a low-grade ferronickel directly in the electric furnace. However, owing to difficulties in selling the product, operations were discontinued.

In the second case, a plant was erected at Webster, N. C., where experiments were conducted on the reduction of garnierite in the electric furnace with coke as a reducing agent. The ores used were garnierite, containing 7.3 percent Ni, and dunite, containing 1.7 percent Ni. About 10 percent of the charge was coke. The product made was a nickel-iron silicide containing 10-30 percent nickel, 20-30 percent silicon, 40-50 percent iron, 5-10 percent aluminum, 3-5 percent chromium, and 3-4 percent carbon, magnesium, sulfur, and phosphorus. The cost of power was prohibitive, and the operations ceased.

In the third instance Paul Girod worked on the production of a nickel silicide from a silicate ore of Ni in 1903 at the plant of Société Anonyme Electrometallurgique Procédés. The product containing 30 percent Ni and 47.20 percent Si. In 1911 experiments were performed at the same works in an attempt to make a ferronickel containing 3-5 percent Si. The power consumption was 6.86 kw.-hr. per lb. of alloy produced. In practice it is believed that the power consumption could be reduced to 1,200 kw.-hr. per ton of ore, or to 4.69 kw.-hr. per lb. of alloy. A table shows that the ore composition includes 8.33 percent NiO, and the product 41.50 percent Ni. (4 refs. are given.)

329. MINING JOURNAL (LONDON). Electrical Nickel Smelting. I. Continuous Electric Smelting of Low-Grade Nickel Ores. Vol. 242, Apr. 9, 1954, pp. 415-416; Metals Rev., vol. 27, No. 6, June 1954, p. 36 (111C).

Describes the structures of ores tested, with preliminary tests and smelting procedures.

330. NISHIMURA, HIDEO. [Researches on Nickel and Nickel-Containing Alloys and Their Development in Japan During 1938.] Japan Nickel Rev., vol. 7, 1939, pp. 120-138; Chem. Abs., vol. 33, 1939, p. 5345^a.

The subject is reviewed.

331. REMIN, V. P., AND GORSHENIN, D. G. [Smelting Nickel-Containing Sponge Iron in an Arc Furnace.] Stal., vol. 7, 1947, pp. 120-123; Chem. Abs., vol. 41, 1947, p. 5801h.

Ni-containing sponge iron was made into high-alloy steel by direct reduction in an arc furnace. Three kinds of sponge were used. Of these, 2 contained 50 and 64.7 percent and the third 88.94 percent of metallic constituents. The high content of sulfur and phosphorus did not hinder the process, as they were removed in the slags. Magnesium slag severely corroded the furnace lining. The first 2 sponges lost considerable Ni (approximately 23.2 percent during melting), but the loss from the third was 2 to 3 times less.

332. SOCIÉTÉ ANONYME "LE NICKEL." [Removing Iron From Ferronickel and Ferrocobalt.] German Patent 494,023, Jan. 28, 1927; Chem. Abs., vol. 24, 1930, p. 2714.

The molten alloy is sprayed by a gas stream into an oxidizing atmosphere, and the partly oxidized

powdered product is separated into metal and oxide by heating with a flux. If the powdered product is not oxidized to the desired degree, it may be further oxidized by roasting or reduced by melting with untreated alloy.

333. SOCIÉTÉ D'ÉLECTROCHIMIE, D'ÉLECTROMÉTALLURGIE ET DES ACIÉRIES ÉLECTRIQUES D'UGINE. Extraction of Nickel From Low-Grade Ores. British Patent 713,713, Aug. 18, 1954; Chem. Abs., vol. 49, No. 4, 1955, p. 2285g.

Nickel is extracted from low-grade ores, as an Fe-Ni alloy, by mixing successive charges of molten ore with molten Fe and periodically withdrawing a part of the metal. Exothermic heat from oxidation of added Si or Al compensates for heat losses. Formation of CO from addition of carbon causes bubbling.

334. STERN, MAX. [Extraction of Nickel From Ores.] German Patent 525,521, Apr. 8, 1926; Chem. Abs., vol. 25, 1931, p. 4511^a.

Nickel is extracted from ores or ore products containing NiO or Ni₂O₃ in the form of Fe-Ni, by liquefying and mixing the ore and Fe, whereby the nickel oxide is reduced, leaving the Ni free to alloy with the excess of Fe.

PYRO TREATMENTS; OXIDIZED ORES AND OXIDES

REDUCTION; GENERAL

335. CARTER, J. E., AND GENSLE, R. K. (assigned to The International Nickel Co. of Canada). Operating Nickel-Reduction Furnaces. U. S. Patent 2,413,215, Dec. 24, 1946; Chem. Abs., vol. 41, 1947, p. 1198b; British Abs., 1950, p. B-1-790.

The efficiency of a Ni-reduction furnace is greatly influenced by the atmosphere within the furnace for any given temperature. If the reducing atmosphere is too lean, the charge of nickel oxide and coke will lose carbon from the surface, forming an impermeable layer of metallic nickel on the surface of the pile. If the reducing atmosphere is too rich, the furnace temperature will be low. Furthermore, determinations of the furnace atmosphere with an Orsat are too slow to provide effective control. To overcome these difficulties the furnace is equipped with an automatic H₂ analyzer.

336. MÜLLER, R. M. [The Use of Serpentine Rocks for the Production of Nickel. II. The Thermal Reduction of Serpentinates and Their Weathering Products.] Berg-u. Hüttenmänn. Monatsch. Montan. Hochschule Leoben., vol. 95, 1950, pp. 129-132 and 155-161 (see Chem. Abs., vol. 44, 1950, p. 9313e.); Chem. Abs., vol. 44, 1950, p. 10626f.

Serpentinates and other ores of very low Ni content (0.21-0.25 percent) are concentrated by fractional reduction in the liquid phase. This is an application of the fact that various metals can be liberated under increasing temperature in sequence. As serpentine has a very high melting point and liquefies only at about 1,550° C., experiments were carried out with different fluxes (CaO, Na₂SO₄, NaF, Na₂AlF₆, CaF₂, MgF₂, CaCl₂, 2NaF·MgF₂, Na₃PO₄, Na₂P₂O₇, and mixtures of them) to lower the melting point. Lowering of the melting point is necessary to find a material that will withstand the attack of the melts; experiments showed that crucibles of Al₂O₃ and MgO are the only materials not attacked at 1,600° C., while SiO₂, BeO, ZrO₂, and zirconium silicate are attacked at 1,500° C. It was possible to obtain a concentration of Ni up to 5 percent, with some ores even up to 20-30

percent. Although the heat consumption in these processes is very high, a practical application may still be economical if magnesia could be recovered from the slags after the metal phase has been removed from the melt.

- 337. SMIRNOV, V. I.** [Shaft Smelting of Oxidized Nickel Ores.] *Tsvetnye Metal*, No. 3, 1940, pp. 66-73; *Chem. Abs.*, vol. 35, 1941, p. 5070^o.

Reducing sulfide smelting of oxidized Ni ores in shaft furnaces was first introduced in Russia in 1934. Several smelters are now in operation. Smirnov discusses several factors accounting for inefficiency and low recovery and suggests improvements, some of which have already been introduced in practice. The improvements suggested are along the following lines: Better preparation of ore; improvements in roasting; control of charge composition and air consumption; control of charge volume; slag control aimed to improve the smelting of acid ores with the use of additions of limestone; use of fluor spar, etc. Other improvements suggested are: Recovery of Ni from the slags, collection of dust, treatment of ores high in Mg, and improvements in the design of the furnaces.

- 338. UBBELOIDE, A. R.** Interface Catalysis in the Reduction of Metallic Oxides. *Trans. Faraday Soc.*, vol. 29, 1933, pp. 532-534; *Chem. Abs.*, vol. 27, 1933, p. 4158.

Interface catalysis is to be expected in the reduction of oxides of Cu, Ni, Pt, Pd, and Pb. Experiments confirm this for Ni and Cu. A similar phenomenon was observed for Pt oxides. No data are available for Pd and Pb. The interface catalysis so far discovered in the reduction of metallic oxides is attributed to the difficulty in forming any intermediate stage in the reduction.

- 339. URAZOV, G. G., AND BOGATSKII, D. P.** [Physicochemical Investigation of Oxidized Ferronickel Ores.] *Compt. rend. acad. sci., U. R. S. S.*, vol. 50, 1947, pp. 61-63 (in English); *Chem. Abs.*, vol. 41, 1947, p. 6850h.

Ufaley, Batamshinsk, and Khalilovo ores from commercial deposits of the middle and southern Urals were investigated by various physicochemical methods of analysis. Nickel was present chiefly in the form of oxidized minerals finely dispersed in the ores and impregnating their various other mineral ingredients. Clearly individualized silicate-oxidized minerals are present in the ores in extremely insignificant amounts; therefore modern methods of selective concentration cannot be applied effectively. A study of the behavior of oxidized ferronickel ores during calcining and reduction shows that their reduction follows the scheme: $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ in a broad temperature range and makes possible, in principle, the selective reduction of Ni from its oxidized minerals present in oxidized ferronickel ores. The percentage composition and thermograms of the three ores are given in detail.

- 340. ———.** [Chemical and Physical Nature of Silicated Nickel Minerals and the Process of Their Calcination and Reduction.] *Compt. rend. acad. sci., U. R. S. S.*, vol. 55, 1947, pp. 837-839 (in English); *Chem. Abs.*, vol. 41, 1947, p. 7338h.

The results of the calcination and reduction of five silicated Ni minerals, nepouite-garnierite from the Ufaley deposit, Ni cerolite, Ni deweylite from Akkerman, nickel-aluminum silicate, and alyrilite from Aidarly, are given, and the authors conclude that the reduction of Ni-silicated minerals is a strongly endothermic process. The minerals can be reduced directly and effectively without appreciable sintering. The reduction to metal temperatures is lower than for ferrous oxide and higher than for magnetic ferric oxide. Silicated Ni-Co ores containing iron oxides should be

subjected to complex reduction because their selective reduction does not insure a high recovery of Ni and Co. (18 refs.).

- 341. VACUUMSCHMELZE GESELLSCHAFT, GRUBER, H., ROHN, W., AND WEBER, O. H.** Reducing Metals Such as Copper and Nickel From Their Oxides or Other Compounds. *British Patent* 294,795, Sept. 22, 1927; *Chem. Abs.*, vol. 23, 1929, p. 1861^o.

Compounds, such as oxides and sulfides, that are capable of being dissociated at elevated temperatures are subjected, in a solid or fused condition, to a vacuum exceeding the dissociation tension corresponding to the temperature of the compounds until dissociation into solid or molten metal and volatile metalloids is completed.

REDUCTION WITH GASEOUS REDUCTANT

- 342. ARKHAROV, V. I., VARSKAYA, A. K., ZHURAVLEVA, M. G., AND CHUFAROV, G. I.** [Reduction of Mixtures of Magnetic Iron Oxide With Nickel and Cobalt Oxides.] *Doklady Akad. Nauk., S. S. S. R.*, vol. 87, 1952, pp. 49-52; *Chem. Abs.*, vol. 47, 1953, p. 5224c.

The phases of Ni, Co, and Fe present at different points in a reduction with carbon monoxide in a closed system were studied, as well as the composition of the gas phases corresponding to different stages in metal reduction; the carbon dioxide content was determined by rapid freezing and decreased regularly with increasing metal reduction, indicating a continuous variation of the solid phase. In the last stages of reduction a metallic phase Fe-Co of variable composition was shown by X-ray examination. In an equimolecular reduction of iron-nickel oxides with carbon monoxide, an initial reduction to metallic Ni was indicated by the carbon dioxide concentration and confirmed by X-ray analysis showing the normal Ni lattice with $a=3.547$ Angstrom units.

- 343. BLELOCH, WILLIAM.** Smelting of Metallic Oxides in a Blast Furnace. *British Patent* 668,128, Mar. 12, 1952; *Chem. Abs.*, vol. 46, 1952, p. 7028c.

The smelting of Fe ores is improved and the fuel is used in an economical manner by the use of an O_2 - CO_2 blast in which the blast contains 45 percent minimum O_2 and 45 percent minimum CO_2 by weight. The process is also applicable to oxides of Co and Ni.

- 344. BOGATSKII, D. P.** [Reduction of Nickel Oxides With Carbon Monoxide.] *Metallurg.*, vol. 13, No. 1, 1938, pp. 84-90; *Chem. Abs.*, vol. 32, 1938, p. 8898⁴.

The reduction of higher oxides of Ni to NiO was detected at 120° C. and proceeded rapidly at 225° C. Reduction of NiO to Ni was detected at 345° C. and increased rapidly with increase of temperature.

- 345. ———.** [Reduction of Nickel Silicate Minerals With Carbon Monoxide.] *Jour. Appl. Chem., U. S. S. R.*, vol. 20, 1947, pp. 81-88 (in Russian) (*see Chem. Abs.*, vol. 41, 1947, p. 11831); *Chem. Abs.*, vol. 41, 1947, p. 7343e.

The degree of reduction of Ni as a function of temperature (600°-900° C.) and duration of reduction (0.5-3.0 hr.) was detailed for several domestic ores, whose analyses are given. In general, reduction is 14.6-43.3 percent complete in one-half hour at 600° C. and 24-51.4 percent complete in 1 hour at 600° C. and increases with higher temperatures and time. However, certain ores high in silica show a substantially lower reduction at 900° C. owing to recalcination. This is not due to sintering but the exothermal effect corresponds to a crystal-grain growth of an unknown mineralogical component. This can be avoided by prior ignition at 900°-950° C., comminution, and then reduc-

tion. Reduction with CO is substantially lower than with H₂.

- 346.** BOGATSKII, D. P. [Reduction of Nickel Silicate Minerals by Hydrogen in Relation to Their Physicochemical Nature.] *Bull. Acad. Sci., U. R. S. S., Classe Sci. Tech.*, 1946, pp. 891-898; *Chem. Abs.*, vol. 41, 1947, p. 1183i.

Reduction by hydrogen gas at 600°, 700°, 800°, and 900° C. for 0.5, 1, 2, 3, and 4 hr. was investigated on 7 domestic Ni minerals of the type of garnierite or Ni-Al silicates with nickel oxide contents from 4.56 to 37.95 percent. Reductions are substantial even at 600° C. and are generally complete at 800°-900° C., with the rate of reduction of silicates much slower than oxides. In 2 instances, prolonged reduction treatment resulted in lowered recovery owing to recombination or recalcination in silicates between 800° and 960° C. This can be avoided by prior calcination above the temperature of incipient exothermal crystallization or by H₂ reduction at lowered temperature.

- 347.** BRASSET & Co., H. A., G. m. b. H. [Obtaining Nickel From Oxidized Iron Ore.] *Belgian Patent* 444,429, Mar. 31, 1942; *Chem. Abs.*, vol. 39, 1945, p. 486⁴.

The ore is heated to 600°-900° C. in a gas mixture, the oxidizing and reducing constituents of which are so proportioned that the mixture reduces only the nickel oxides. The reduced Ni is converted by CO into nickel carbonyl, which is later decomposed, yielding Ni metal.

- 348.** BROGDON, V. H. (assigned to Nicaro Nickel Co.). Recovery of Nickel and/or Cobalt From Ores. U. S. Patent 2,400,098, May 14, 1946; *Chem. Abs.*, vol. 40, 1946, p. 4337⁸.

Hydrous silicate Ni and Fe ores are heated to a temperature of 1,400° F. The controlled simultaneous decomposition and reduction of hydrous silicate ore are carried out by a gradual increase in temperature in the range between 1,000° (or 1,200°) and 1,400° F., where the rate of increase must not be greater than 6° F. per min. and is preferably kept at 2°-6° F. per min. The gases employed in the reaction are mixtures of producer gas and combustion gases, the ratios CO:CO₂ and H₂:H₂O being variable in the volumetric range ratios of 30-70; 70-30. The removal of the reduced metal is carried out with an ammoniacal leaching liquor. Yields from various low-grade (Cuban) ores (lateritic serpentine and limonite types) are reported as 90-95 percent.

- 349.** CARON, M. H. [Extraction of Nickel and Cobalt From Oxidic Ores.] *Netherlands Patent* 44,768, Jan. 16, 1939 (*see French Patent* 837,609, Feb. 15, 1939; *Chem. Abs.*, vol. 33, 1939, p. 5797⁸); *Chem. Abs.*, vol. 33, 1939, pp. 2867⁹ and 4183⁹.

In the reduction of nickel, iron, or cobalt hydrosilicates at 950°, 700°, or 1,000° C. with H₂ or CO, a ratio of H₂ to H₂O or of CO to CO₂ of less than 1 decreases adsorption of gas by the reduced metal. The addition of small amounts of S, Se, Te, and As to the ore also prevents excessive gas sorption. The atmosphere should be adjusted during cooling so that no H₂ or CO is taken up. The treated ore is chilled in water when cooled to 180° C. to prevent carbonyl formation.

- 350.** FALCONBRIDGE NIKKELVERK, A. S. Reducing Oxides of Nickel, etc. *British Patent* 423,951, Feb. 12, 1935 (*see German Patent* 598,334; *Chem. Abs.*, vol. 28, 1934, p. 5392²); *Chem. Abs.*, vol. 29, 1935, p. 5062².

An oxygenated compound of Ni is reduced at a temperature below the sintering point (for example, at 400°-500° C.) by treatment with a reducing gas preheated, for example, to 500°-700° C.

- 351.** ———. [Gaseous Reduction of Oxidic Nickel or Nickel-Copper Compounds.] *Norwegian Patent* 54,138, July 9, 1934; *Chem. Abs.*, vol. 29, 1935, p. 5804¹.

Before being introduced into the reducing furnace, the reducing gas is preheated to a temperature considerably above that at which the reduction of the NiO is conducted.

- 352.** GUSTAFSSON, E. G. T. [Sponge Metals.] *Swedish Patent* 76,102, Dec. 20, 1932; *Chem. Abs.*, vol. 27, 1933, pp. 2659 and 5300.

Sponge Fe, Co, Ni, Cr, Cr-Fe, or other metal is produced from ores or other oxidic raw materials by reduction without melting. The finely ground ore and excess of finely divided reducing agent are mixed intimately, with a suitable binder, if necessary, and the mixture is made into briquets or other form. This product is heated by means of hot combustion gases containing enough O₂ to burn part of the excess reducing agent. (*Swedish Patent* 76,104, Dec. 20, 1932.) The above process is carried out without briquetting the mixture until reduction is nearly complete. Final reduction to the desired extent is effected in another furnace or another part of the same furnace, without contact with combustion gases, by indirect heating of the charge.

- 353.** ———. [Sponge Metal.] *Swedish Patent* 78,764, Oct. 31, 1933 (*see Chem. Abs.*, vol. 27, 1933, p. 5300); *Chem. Abs.*, vol. 28, 1934, p. 1979⁴.

Sponge Fe, Co, Ni, or ferrochrome is produced by reducing the oxidic ores by a reducing gas in a furnace in which the charge is in continuous motion in opposite direction to the gas. Powdered coal or other carbonaceous material is added to the gas before it is introduced into the combustion zone of the furnace in such amounts that, during the last critical stage, the ore is reduced in the presence of such carbonaceous materials.

- 354.** HILLS, R. C., AND DUFOUR, M. F. (assigned to Nicaro Nickel Co.). Recovery of Nickel and/or Cobalt From Nickeliferous Ores. U. S. Patent 2,400,115, May 14, 1946; *Chem. Abs.*, vol. 40, 1946, p. 4338¹.

The process is especially applicable to low-grade (for example, Cuban) ores where recovery practice employed for high-grade ores would not be economically feasible. The ore is first subjected to a reducing treatment whereby at least 85 percent of the Ni and most of the Co are reduced to the metallic state. Iron which has been reduced in part must be reoxidized in a steam-CO₂ stream. The reduction may be carried out 60 to 200 minutes with producer gas, at 1,000°-1,400° F., where the temperature should be increased at the rate of 6°-10° F. per minute. The reoxidation is carried out by introducing steam at 700°-800° F. for 15 minutes, during which time the temperature falls to 400°-500° F. If CO₂ is employed, it is introduced at 1,100° F. for 20-60 minutes. This reoxidation is aimed selectively at the Fe, which has been reduced previously. The cooled mass is then extracted in an aqueous ammoniacal solution. Reported yields on a limonitic ore containing Fe₂O₃ 72.05, Ni oxide 1.57, Co oxide 0.12 percent, and other noninterfering minerals were Ni 90.2 and Co 68.0 percent.

- 355.** ——— (assigned to Nicaro Nickel Co.). Reduction of Ores Containing Nickel. U. S. Patent 2,473,795, June 21, 1949; *Chem. Abs.*, vol. 43, 1949, p. 6562e.

Nickel is recovered from nickeliferous lateritic ores by the reduction of NiO to Ni, without, however, the reduction of the iron oxides. This is achieved by controlling the CO₂/CO ratio (K value) and adjustment of the temperature to permit reduction of the NiO se-

lectively. The K values for the systems $\text{Fe}_3\text{O}_4\text{-NiO}$, $\text{Fe}_3\text{O}_4\text{-Ni}$, FeO-Ni , and Fe-Ni are given as a function of temperature. A continuous furnace is described in which the ore is fed in on top and falls over rotating tables to the bottom exit. Oil and air are fed through combustion and mixing chambers, with producer gas from the bottom, at 4 stages along the ore passage; the optimum operating temperatures range from $100^\circ\text{--}1,300^\circ\text{F.}$, and K from about 2 to 6.

356. KALMUS, H. T. Preparation of Metallic Cobalt by Reduction of the Oxide. Canadian Dept. of Mines, Mines Branch Rept. 259, 1912, pp. 1-36, Bureau of Mines Inf. Circ. 6331, p. 31.

357. KIVNICK, A., AND HIXSON, A. N. Reduction of Nickel Oxide in Fluidized Bed. Chem. Eng. Progress, vol. 48, No. 8, August 1952, pp. 394-400; Eng. Index, 1952, p. 675.

Experiments were conducted to determine the rate of reduction of finely divided nickel oxide by hydrogen. The results indicate that the overall reaction rate is affected both by a kinetic reaction step and by a diffusional or mass transfer. The process may find industrial use for preparing pure Ni from the oxide. One run resulted in 75 percent metallic Ni. Bibliography included.

358. MOND NICKEL CO. Reduction of Metallic Oxides. British Patent 686,921, Feb. 4, 1953; Chem. Abs., vol. 47, 1953, p. 68521.

The final reduction of roasted Cu and Ni matte is facilitated by a preliminary partial reduction of the oxides with CH_4 . Crushed calcines pass downward through a vertical pipe heated from the outside while natural gas is allowed to pass through them counter-currently. At $580^\circ\text{--}1040^\circ\text{C.}$ the oxides are reduced at least 88 percent, and about 1-5 percent C is deposited on the metal, which is cooled by incoming cold gas and water circulating around the lower portion of the reduction pipe.

359. MUKOYAMA, MIKIO, AND TAKEL, TAKESHI (assigned to the Minister of Commerce and Industry). [Selective Separation of Nickel-Cobalt Silicate.] Japanese Patent 181,477, Jan. 23, 1950; Chem. Abs., vol. 46, 1952, p. 1423f.

The above patent covers the treatment of garnierite with an iron ore so that the nickel-iron ratio is 1-4, heating, cooling, magnetic separation, and leaching with sulfuric acid.

360. N. V. MAATSCHAPPIJ VOOR ZWAVELZUURBEREIDING VOORHEEN G. T. KETJEN & Co. [Recovery of Metals From Ores.] French Patent 815,321, July 9, 1937; Chem. Abs., vol. 32, 1938, p. 1637⁹.

Oxide ores and silicates containing metals with lower heats of combustion than iron are treated. They are heated with a reducing gas or gases at such a temperature that only the metals of lower heat of combustion, such as Ni, are brought to the metallic form. The capacity for extraction may be increased by adding C or some other element more electropositive than the metals to be extracted and recovering these metals by use of an electrolyte. Steam may be added to the reducing gases.

361. PARRAVANO, G. Reduction of Nickel Oxide by Hydrogen. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 1194-1198; British Abs., 1952, p. A-1-554.

The reduction of NiO by H_2 was studied at $150^\circ\text{--}350^\circ\text{C.}$ and initial pressures of H_2 of 200-500 mm. The addition of foreign ions to NiO affects both the rate and activity energy of reduction, and these effects are related to the change in its electronic properties.

362. PLANIOL, RÉNÉ. Reduction of Metal Oxides. British Patent 646,789, Nov. 29, 1950; Chem. Abs., vol. 45, 1951, p. 3789e.

Easily reducible metal oxides are reduced in two stages—(1) heating in a nonreducing atmosphere to produce Fe_3O_4 , and (2) heating in H_2 at elevated temperatures to form dense metallic iron.

363. QUENEAU, P. E., BORLAND, J. H., AND RENZONI, L. S. (assigned to International Nickel Co.). Treatment of Nickel-Containing Ores. U. S. Patent 2,478,942, Aug. 16, 1949 (see German Patent 823,348, Dec. 3, 1951 (*Cl. 40a 43₃₀*), Chem. Abs., vol. 49, 1955, p. 144a; and British Patent 646,488, Chem. Abs., vol. 45, 1951, p. 3788e); Chem. Abs., vol. 43, 1949, p. 8343h.

An improvement on the ammonia leaching process for lateritic limonite ores containing small quantities of Ni is described. In the reduction-oxidation, re-reduction process temperature limits of $1,200^\circ$ to $1,600^\circ\text{F.}$ are maintained, as above $1,600^\circ\text{F.}$ the Ni recovery suffers owing to formation of an antigorite. The ore is sufficiently comminuted, reduced to a point where substantially all of the Ni is soluble, then oxidized, and re-reduced to render the Fe insoluble. After cooling the reduced ore is immersed in a leaching solution in which substantially all of the Ni values dissolve, but in which the bulk of the undesirable mineral matter will remain insoluble. After removal of the insolubles, Ni is recovered by known methods.

364. RACINE, JEAN. [Study of the Reducing Properties of Methane.] Compt. rend., vol. 220, 1945, pp. 823-825; Chem. Abs., vol. 40, 1946, p. 36724.

The reduction of metallic oxides by methane was studied in the temperature range up to $1,100^\circ\text{C.}$ Various metallic oxides are reported on. Cobaltic oxide is reduced to cobaltous oxide at 450°C. and to Co metal at 800°C. ; a carbide is formed at $1,000^\circ\text{C.}$ Nickelous oxide is reduced to metal at 590°C. Acetylene and C appear at 830°C.

365. SLOMNECO-BANGERTER, N. [Iron, etc.] Swiss Patent 195,117, Apr. 1, 1938 (*Cl 75a*), Chem. Abs., vol. 32, 1938, p. 7010⁷.

Metals of the Fe group, that is the eighth group of the periodic table, are obtained by fusing their oxides with the aid of a SiO_2 flux, and reducing them to the metal by gaseous reducing agents such as CO or H_2 .

366. TAYLOR, G. B., AND STARKWEATHER, H. W. Reduction of Metal Oxides by Hydrogen. Jour. Am. Chem. Soc., vol. 52, 1930, pp. 2314-2325; Chem. Abs., vol. 24, 1930, p. 3944⁹.

Describes a method for studying the rate of reduction of metal oxides at temperatures below 500°C. in which the volume of H_2 consumed is measured. The oxides of Ni, Cu, Fe, and Zn were studied by this method. Fe_3O_4 gel is reduced to ferroso-ferric oxide at 350°C. and to metallic Fe at 450°C. Ignited Fe_3O_4 is not appreciably reduced at 350°C. but goes to metal at 450°C. Foreign metal interfaces with Fe_3O_4 accelerate the reduction of Fe. Alumina and Cr_2O_3 greatly retard the reduction of ferroso-ferric oxide. Fe_3O_4 gels show the glow phenomenon in H_2 at fairly low temperatures but not in air or vacuum.

367. TSCHOP, H. E., CARTER, J. E., AND GOODRICH, C. B. (assigned to International Nickel Co., Inc.). Reduction of Metal Oxides. U. S. Patent 2,663,631, Dec. 22, 1953; Chem. Abs., vol. 48, 1954, p. 6364e.

A method is disclosed for partial reduction of oxides of Ni, Cu, and Co with hydrocarbon gases (natural gas) in a vertical annular furnace. During the reduction a controlled amount of highly active C is deposited on the partly reduced charge, which completes the reduction to the metal in an electric arc or induction furnace without further addition of reducing agents. In the primary reduction step descending oxide of 0.1-0.5-inch diameter is reduced to a high metal content by an ascending flow of natural gas.

The charge is preheated to 1,100° F., and reduction begins in a zone between 1,100° and 1,700° F. with the major portion effected between 1,700° and 1,900° F. Further reduction is obtained as the cooler natural gas contacts the hot charge, with simultaneous deposition of finely divided active C particles between 1,700° and 1,100° F. The C content of the charge is controlled within 0.4-4 percent. Furnaces with reduction mullies of over 5-inch diameter require external and internal heating. The ratio of heating surface area to effective annular volume is maintained at 0.4-0.5.

368. UHDE, FRIEDRICH. [Reducing Metal Compounds.] French Patent 776,588, Jan. 29, 1935; Chem. Abs., vol. 29, 1935, p. 3292².

Compounds such as oxides, carbonates, and nitrates of Cu, Sn, Zn, Cd, Fe, Co, and Ni are reduced at relatively low temperature by means of gaseous hydrocarbons, by first causing the hydrocarbons to react with the used reduction gases. Oxygen compounds are partly removed from the used gases before causing them to react with the hydrocarbons.

369. WITTER, WILHELM (assigned to Firma M. Lissauer et Cie.). Recovering Nonferrous Metals From Melts Containing Oxides. U. S. Patent 1,941,506, Jan. 2, 1934; Chem. Abs., vol. 28, 1934, p. 1649³.

Material containing oxides such as those of Cu, Ni, Sn, Pb, Bi, and Sb is melted, and reducing gases are passed through the molten material while it is heated in a furnace in which the heating gases are introduced from above the melt; the interaction between the reducing gases and the combustion gases is so regulated that a neutral or slightly reducing atmosphere obtains at the surface of the melt, to effect recovery of Cu and Ni present wholly and Sn, Pb, Bi, and Sb at least partly in reguline form.

REDUCTION WITH SOLID REDUCTANT

370. BASSET, L. P. [Reducing Metal Oxides, Carbonates, Sulfates, etc.]. German Patent 485,430, June 23, 1920 (see German Patent 484,287); Chem. Abs., vol. 24, 1930, p. 817².

The oxides, etc., are mixed with a flux and the necessary amount of C for reduction, and the mixture is heated with a reducing flame. The flame may be produced from powdered coal or oil and a restricted amount of compressed and highly heated air. The products may be metals, alloys, or compounds, this depending on the initial materials. The manufacture of Cr, Mn, Si, Ti, Mo, V, Ni, and P and their alloys or compounds with one another and with Fe, and the manufacture of CaC₂ and alkali or alkaline earth sulfides are referred to. The manufacture of Fe or steel is excluded.

371. BAUKLOH, W., AND SPRINGORUM, F. [Reduction of Nickel and Copper Oxides With Solid Carbon.] Ztschr. anorg. allgem. Chem., vol. 230, 1937, pp. 315-320 (see Chem. Abs., vol. 25, 1931, p. 4498); Chem. Abs., vol. 31, 1937, p. 2113³.

Powdered mixtures of metal oxides were heated with gas-free Ceylon graphite. At 550° C., the first reduction of CuO was observed. Reduction of NiO begins at 800° C. Results with Ni₂O₃ are similar. Nickel oxides can be completely reduced.

372. BOGATSKII, D. P. (Institute of General Inorganic Chemistry and Institute of Nonferrous Metals, Moscow). [Direct Reduction of Oxidized and Silicate-Oxidized Nickel-Cobalt Ores.] Bull. Acad. Sci.

U. R. S. S., Classe Sci. Tech., 1946, pp. 1809-1822 (in Russian); Chem. Abs., vol. 41, 1947, p. 3408g.

The expulsion of contained water in the ore, water of crystallization, or zeolitic water is indicated at different temperatures in reduction experiments with C for several ores studied. Results of direct reduction with H₂ and CO are given in terms of Fe, percentage of Ni in the reduction products, and percentage of the contained Ni reduced at temperatures from 100° to 1,000° C. with either H₂ or CO, or a half-and-half mixture of CO with CO₂. Nickel oxide not combined as silicate is reduced as low as 300° C. with complete reduction at 600°-700° C., as silicate complete reduction occurs at 900°-1,100° C. Ni reduced by H₂ has a much higher reactivity than that reduced by CO and C.

373. ———. [Calcination and Reduction of Nickel Hydrosilicates by Carbon.] Izvest. Akad. Nauk. S. S. R. Otdel. Tekh. Nauk., 1949, pp. 1512-1525; Chem. Abs., vol. 45, 1951, p. 9435c.

The reduction of silicate minerals of Ni by C was studied experimentally from the following points of view: (1) The physicochemical transformations in the process of warming and calcination of these minerals before their reduction; (2) conditions of carrying out the process; (3) the relation between reaction rate and the conditions for carrying out the reduction with C; and (4) development of optimum conditions for maximum reduction of these minerals by C. The heating and calcination tests showed that: (1) The process of reduction of Ni from its silicate-oxide minerals is highly endothermic and proceeds to a marked degree in the high-temperature region, in contrast to the reduction of nickelous oxide; (2) reduction by C begins in the higher temperature region in contrast to processes with H₂ or CO (hygroscopic and constitutional water is removed completely at the beginning of the reduction process); (3) reduction of the nickel hydrosilicates by C is much slower than that of nickelous oxide; and (4) reduction of the nickel silicate-oxides is not complete up to their sintering temperature. A table gives data for each Ni mineral studied, temperature of the process of reduction, length of time of the reduction, percentage yield of Ni, and percentage extent of reduction. Data are also given in graphical form.

374. ———. [Investigation of the Processes of Calcination and Reduction of Nickel Hydrosilicates by Carbon.] (In Russian.) Izvestiya Akademii Nauk. S. S. R. (Bull. Acad. Sci., U. R. S. S.), Classe Sci. Tech., October 1949, pp. 1512-1525; Metals Rev., vol. 24, No. 3, March 1950, p. 19 (48B).

The subject was experimentally investigated from several theoretical and practical viewpoints. The methods of investigation and data are discussed.

375. EPISHIN, P. S. [Obtaining Powdered Nickel for the Production of Nickel Sulfate in the Ufael Nickel Plant.] Inf. Tekh. Sbornik Soyuznikel' olovoproekt. No. 1, 1940; pp. 37-40; Khim. Referat. Zhur., No. 9, 1940, p. 74; Chem. Abs., vol. 37, 1943, p. 1018³.

Nickel oxide and charcoal are placed in a flask in layers. The reduction is carried out at 900°-1,100° C. until all the Ni is fused. The time required is 2.5-3.0 hr. for the upper and middle layers and 3.0-3.5 hr. for the lower part of the flask. Approximately 15-20 minutes before the mass is discharged, the Ni is covered with charcoal, and the mass is plunged into water, washed free from charcoal, and dried. The method requires 40 percent less fuel.

376. FLANNERY, J. W. Carbon-Free Elements From Ores of Iron, Chromium, Manganese, and Nickel Oxides. U. S. Patent 1,983,604, Dec. 11, 1935; Chem. Abs., vol. 29, 1935, p. 715¹.

For producing refined, substantially C-free metal from Fe, Cr, Mn, and nickel oxide ores, the ore is mixed with reducing and fluxing materials including a proportion of C substantially the equivalent of the O combined with the metal to be reduced, and fluxing substances such as Na_2CO_3 and CaO are used, which form a soft, pasty, viscous mass with the gangue of the ore. The temperature used is below that at which the C will combine with the O_2 of the furnace atmosphere. The mixture is so heated that a liquid slag is formed before the melting point of the pure metal is reached. The metal as it melts passes through the slag to the bottom of the furnace.

377. FLODIN, H. G., AND GUSTAFSSON, E. G. T. [Production of Metals of Iron Group.] Swedish Patent 67,175, Apr. 16, 1929; Chem. Abs., vol. 24, 1930, p. 1304¹.

Metals belonging to the Fe group (Fe, Co, Ni, and Mn) or alloys of such metals are produced by mixing ores or other oxidic raw materials with finely divided reducing agents, such as carbonaceous materials, iron sulfides or materials containing iron sulfides, with or without a binding substance, preferably a carbonaceous or calciferous material, and heating in a suitable electric furnace with exclusion of air. The charges serve as the resistance.

378. HERAEUS-VACUUMSCHMELZE, A. G., AND ROHN, WILHELM. [Reduction of Oxides.] German Patent 600,369, Sept. 29, 1934 (*Cl. 40a 11.55*); Chem. Abs., vol. 29, 1935, p. 442⁶.

Zirconium is made by causing a carbide of Zr to react with ZrO_2 in a bath of fused Zr under reduced pressure; Si, Ti, Hf, Th, V, Ni, Cr, and Mo are obtained similarly from the corresponding oxides and carbides in baths of the fused elements.

379. IWANCIW, EMILIAN. [The Effect of Pressure on the Reduction Process of Metal Oxides by Carbon.] Arch. Gornictwa i Hutnictwa, vol. 1, 1953, pp. 131-180; Chem. Abs., vol. 48, 1954, p. 13,578i.

The investigation of the reduction process was carried out with two materials, NiO and Fe_2O_3 . According to Iwanciw, the reduction proceeds in three separate stages, (1) $\text{MO} + \text{CO} = \text{M} + \text{CO}_2$; (2) Boudouard's reaction $\text{CO}_2 + \text{C} = 2\text{CO}$; and (3) "fissure diffusion" of CO and CO_2 throughout the reduced metal. The layer of metal produced in the first stage is not uniform but has numerous fissures because of the density changes during the process of reduction from MO to M. These fissures are responsible for the penetration of the reducing gases to the unreduced parts and for the outflow of the gaseous product of reduction, CO_2 . The experimental data show a definite effect of the temperature on the rate and degree of reduction, both of which increase with increasing temperature. The effect of the change in pressure between 1 and 3 atmospheres is very slight. There is a considerable deceleration of the reduction process near the absolute vacuum. The latter clearly indicates the gaseous character of the reduction process. The maximum reduction rate of the metal oxides within a given temperature range corresponds to an optimum pressure P equal to the sum of the partial pressures of CO and CO_2 of the reduction system. The values of P show a tendency to increase with increasing temperatures. (32 refs.)

380. KRUPKOWSKI, A. [The Reduction of Metallic Oxides by Charcoal and Coke: CuO , Cu_2O , NiO, and Fe_2O_3 .] Ann. acad. sci. tech. Varsovie, vol. 3, 1936, pp. 238-263; Chim. et ind., vol. 38, pp. 899-900 (*see* Chem. Abs., vol. 30, 1936, p. 8115⁵); Chem. Abs., vol. 32, 1938, p. 2065⁴.

Charcoal reduces CuO and Cu_2O to $\text{Cu} + \text{CO}_2$; both reactions are exothermic, the first starting at 680°C . and the second at 620°C . Similarly, charcoal reduces

NiO to Ni and CO_2 ; the reaction is endothermic and offers isothermic characteristics; it occurs at 790°C . The higher temperature of isothermic reduction is sharply apparent. There is close relationship between this temperature and the rules of chemical kinetics. The reduction of Fe_2O_3 by charcoal is also discussed.

381. MEYER, R. F. (assigned to Meyer Mineral Separation Co.). Treating Oxidized Ores Such as Ores of Iron, Nickel, and Chromium. U. S. Patent 1,898,018, Feb. 21, 1933; Chem. Abs., vol. 27, 1933, p. 2659.

Oxidized ore containing reagent metal or transition elements is heated with a combustible reducing agent such as coal in an atmosphere containing SO_2 ; and then cooled with the exclusion of O_2 , producing a "reagent metal" compound in lower valent form highly reactive to acidic gases and stable toward moisture, and metal values are then extracted by treating the material with acidic gases, such as Cl_2 .

382. MUKOYAMA, MIKIO (assigned to the Minister of Commerce and Industry). [Metallic Cobalt, Nickel.] Japanese Patents 181,475 and 181,476, Jan. 23, 1950; Chem. Abs., vol. 46, 1952, p. 1424i.

Cobalt oxide or NiO is molded with C, alkali carbonate, and alkaline-earth metal and reduced at red heat by the accelerating action of the carbonate to a sponge-form Co or Ni.

383. SANTOS, T. D. S. (University of São Paulo, Brazil). [Preliminary Notes on Extraction of Cobalt, Nickel, and Copper From Manganiferous Ores of Niquelândia, Goiaz, Brazil.] ABM, Bol. assoc. brasil. metais., São Paulo, vol. 10, 1954, pp. 221-230; Chem. Abs., vol. 49, 1955, p. 13044e.

The ore, containing MnO_2 44.8, Fe_2O_3 13.7, SiO_2 5.6, CoO 4.8, NiO 2.9, and CuO 2.3 percent, was smelted with waste pyrite and charcoal in presence of fluxes. Small quantities were used with waste pyrites obtained from washing coals of Santa Catarina. The wastes contained FeS_2 71 and C 13 percent. The fluxes were sand, containing SiO_2 98.5 percent, and limestone, containing CaO 52 percent. The charge was composed of ore 500, sand 250, limestone 260, charcoal 40, and waste pyrite 110 gm. The produced metal contained Co 10.3, Ni 11.0, and Cu 12.2 percent, with yields for Co 38.6, for Ni 67.2, and for Cu 94.0 percent. This enrichment was due to priority in the reduction of CoO , NiO, and CuO over the reduction of MnO_2 .

384. TAFEL, VICTOR, AND KLEWATA, FRITZ. [Reactions in the Metallurgy of Nickel Stone Containing Copper.] Metall. u. Erz., vol. 27, 1930, pp. 85-88; Chem. Abs., vol. 24, 1930, p. 2089.

A study of the reaction between Cu_2S and NiO at various temperatures led to the conclusion that at about $1,300^\circ\text{C}$. the production of metallic Cu and Ni occurs as follows: $\text{Cu}_2\text{S} + 2\text{NiO} \rightarrow 2\text{Cu} + 2\text{Ni} + \text{SO}_2$ —65.4 kcal. Values of $\log K$ were determined from the equation

$$\log K = \frac{65,400}{4,571 T} - 1.75 \log T - 3.3, \text{ and give } \log K = 0 \text{ at about } 1,330^\circ\text{C}.$$

The SO_2 pressure is then 1 atmosphere at this temperature, and the reaction can proceed as in the equation above. In the converter the NiO formed is considered to be in "statu nascendi" and immediately reacts with Cu_2S . All substances which might form a slag with NiO must be carefully excluded, thus ruling out an acid lining in the converter.

ROASTING WITH A SALT OR SALT-FORMING GAS

385. BERDNIKOV, A. E. [Chlorination of Lean Oxidized Nickel Ores by Elementary Chlorine.] Tsvetnye

Metal, No. 9, 1938, pp. 91-94; Chem. Abs., vol. 33, 1939, p. 2857⁴.

The author's laboratory experiments showed the feasibility of extracting Ni from oxidized ores containing 1 percent Ni or less. A recovery of 78-82 percent of the contained Ni is claimed possible, with consumption of coal or charcoal (for reducer) at 20-25 percent of the weight of the ore. If Co is present in the ore, it is converted to chloride with the Ni and can be easily separated from the solution. Only 3 or 4 percent of the Ural Ni ores (with Ni content above 1 percent) can be extracted by pyrometallurgical means; the chlorination method is therefore of great promise in the treatment of lean Ni ores.

386. BOGATSKII, D. P. [Chlorination of Silicate-Oxide Nickel Ores.] Jour. Appl. Chem., U. S. S. R., vol. 17, 1944, pp. 346-353; Chem. Abs., vol. 39, 1945, p. 2951²; British Chem. Abs., 1945, p. B-1-328.

The silicate-oxide Ni ores can be effectively worked by means of chlorination. The silicate fraction is more difficult to chlorinate than is the nickel oxide. Complete chlorination of the silicate (garnierite) requires a temperature of 1,100°-1,150° C. Up to 96.7 percent of the Ni can be recovered. The method appears to be independent of Ni concentration in the ore and is thus feasible for the treatment of lean ores. Moisture does not have an adverse effect on chlorination. At 800° C. complete volatilization of nickel chloride was observed. Simultaneous reduction with C and chlorination at 400°-500° C., followed by leaching with H₂O or chlorination in the presence of C at 800° C., with volatilization and condensation of the chlorides is recommended. Co can be recovered from the ore under the same conditions.

387. ———. [Chlorination of Garnierite.] Compt. rend. acad. sci., U. R. S. S., vol. 45, 1944, pp. 67-68; Chem. Abs., vol. 40, 1946, p. 4632⁴.

Chlorination commences at about 280° C. and NiCl₂ begins to volatilize at about 400° C., but complete extraction of Ni is obtained only in the temperature range 1,100°-1,150° C.; this temperature is lowered to about 900° C. by preliminary reduction with H₂ or C.

388. BROWN, E. H., AND BRODERICK, S. J. (Bethlehem Mines Corp.). Treating Nickeliferous Iron Ores. U. S. Patent 2,067,874, Jan. 12, 1937; Chem. Abs., vol. 31, 1937, p. 1342¹.

A selective low-temperature reduction of the ore is effected under conditions (such as the use of H₂ at about 600° C.) favoring complete reduction of the Ni without substantial reduction of the Fe. The reduced Fe and Ni are chlorinated at a temperature (suitably about 200° C. or lower) favorable to the complete conversion of a reduced Ni to soluble chloride and some conversion of the reduced Fe to chloride. The chlorinated product is leached with hot water at a temperature (suitably about 85° C.) at which the solubility of the iron chloride is at a minimum, but the high solubility of the nickel chloride is unaffected.

389. DE ARAUJO, H. E. [The Study of the Metallurgy of Nickel in Brazil.] Rev. soc. brasil. chim., vol. 2, 1931, pp. 438-441; Chem. Abs., vol. 26, 1932, p. 2677.

A new process is contemplated whereby garnierite is treated to give a nickel sulfide and iron sulfide matte. The ore is fused with lime and gypsum. The gypsum is reduced to the sulfide and converts the nickel silicates of the ore into the sulfide with calcium silicate becoming the slag. The nickel sulfide is stable throughout the process. An excess of lime is advisable to neutralize any excess silica and to keep the slag with the minimum amounts of Ni and Fe. The matte of the composition, Fe 30-40 percent, Ni 30-40 percent, and S 25-28 percent is melted and placed in a Bessemer converter where air is blown through the mass for a pe-

riod of 1½-2 hr. per ton of material. The iron sulfides are oxidized and react with an added amount of silica to form iron silicate slag, the nickel sulfides being unaffected. The nickel sulfide is placed in a reverberatory furnace and after 2 to 3 days the resulting oxides are reduced, and the Ni is purified electrolytically. The best fusion mixture was found to contain SiO₂ 48-50, Al₂O₃ 14-15, CaO 18-20, MgO 6-7, Ni 0.5-0.6, and Fe 2-3 percent and fuses at 1,350° C. An excess of silica lowers the point of fusion, gives a purer Ni matte, and reduces the amount of fuel necessary for the process.

390. HART, CHARLES (one-half to Peter Shields). Chloridizing and Volatilizing Process for Separating Chromium, Iron, and Nickel From Ores. U. S. Patent 2,030,868, Feb. 18, 1936; Chem. Abs., vol. 30, 1936, p. 2160².

Ni and Fe from ores containing Ni, Fe, Cr, silica, and alumina are reduced to sponge with a limited amount of C, chlorinated; in a second step the residue is treated with more carbon for a longer period to reduce the combined chromium to metal, which is also chloridized and volatilized, leaving silica and alumina in the residue.

391. ———. Chloridizing and Volatilizing Process for Separating Iron and Nickel From Oxide Ores. U. S. Patent 2,030,867, Feb. 18, 1936 (see Canadian Patent 363,253, Jan. 5, 1937; Chem. Abs., vol. 31, 1937, p. 1342¹); Chem. Abs., vol. 30, 1936, p. 2161².

The ore is reduced to sponge metal in the presence of a limited quantity of C and at a temperature not substantially exceeding 1,000° C. The reduced ore is treated with Cl₂ at a temperature of 200°-500° C. for chlorinating elemental Fe and Ni and for a time sufficient for selective elimination of elemental Fe as FeCl₃. The ore is then heated in the presence of Cl₂ to 700°-900° C. for completing chlorination of elemental Fe and Ni and for a time sufficient to eliminate them as vapors. During this operation, the quantity of C is restricted sufficiently, so that no substantial amount is present during chlorination of the ore. The mixed vapors are removed and cooled to 420°-700° C. for effecting deposition of nickel chloride from the vapors.

392. KLYACHKO-GORVICH, L. L., BULGAKOVA, T. I., AND GERASIMOV, Y. I. [Interaction of Cobalt Oxides With Sulfur Oxides.] Zhur. Obschel. Khim. (Jour. Gen. Chem.), vol. 18, 1948, pp. 1580-1589; Chem. Abs., vol. 43, 1949, p. 6931g.

Pure cobalt oxide or nickelous oxide is completely converted to sulfate at 600° C. by repeatedly pulverizing the compounds in the presence of mixtures of sulfur dioxide and O₂. However, it is simpler to carry out the reaction not quite to completion without pulverizing, and to extract the sulfates formed with water. Ferric oxide is a catalyst for the reaction. Data are given for the vapor pressures of the sulfates at various temperatures.

393. LEBEDEV, P. S. [Sublimation Method for Obtaining Pure Metals From Ores.] Sbornik Trudov Moskov. Inst. Stal. Novoe Tekhnol. Protzessakh Metallurg. Proizvodstva, 1935, pp. 5-91; Chem. Abs., vol. 30, 1936, p. 2886².

Starting with oxides of metals, or, in some instances, ores, a chlorination is performed by heating with coal or coke while introducing chlorine gas or hydrochloric acid. The chlorides are distilled, sometimes fractionally, and finally the molten chloride of the metal is electrolyzed, producing pure metal. This treatment, used for Ni among a long list of other metals, is modified for each specific metal. Temperatures and conditions are specified for this procedure, together with information on various metal phases and compounds and corresponding temperatures.

394. MEYER, R. F. (assigned to Meyer Mineral Separation Co.). Treating Oxidized Ores Such as Those of

Nickel, Cobalt, Copper, Iron, Precious Metals, etc. U. S. Patent 1,988,015, Jan. 15, 1935 (see Chem. Abs., vol. 28, 1934, p. 87¹); Chem. Abs., vol. 29, 1935, p. 1376¹.

The ore to be treated is substantially free from S and may contain Ni, Co, Cu, Fe, or precious metals. It is mixed with a solid sulfur-containing material such as iron pyrite and reduced at 350°–800° C. in a reducing atmosphere and allowed to cool in a nonoxidizing atmosphere. It is now in a state readily amenable to recovery of metal values as by chloridation and extraction.

395. MEYER MINERAL SEPARATION Co. [Treating Ores.] German Patent 602,277, Sept. 5, 1934 (*Cl. 40a 2.60*); French Patent 743,985, Apr. 10, 1933; Chem. Abs., vol. 27, 1933, p. 3905 (see U. S. Patent 1,833,684, Nov. 24, 1932, Chem. Abs., vol. 26, 1932, p. 952); Chem. Abs., vol. 29, 1935, p. 438¹.

Dry oxide ores of Cu, Ni, etc., containing Fe are heated to 450°–600° C. with a reducing agent, whereby an active form of FeO is produced. The product is cooled in an inert or reducing atmosphere and then treated at 200°–300° C. with Cl₂ or a gas containing Cl₂, for example, HCl or FeCl₃ vapor. FeCl₃ is formed and converts the Cu, Ni, or other desired metal in the ore into chloride. The final product contains only a little Fe in water-soluble form. Gives numerous details and describes specific processes.

396. MOROSOV, I. S., URAZOV, G. G., AND EFREMOV, A. N. [Chlorination of Low-Grade Copper-Nickel Ore.] Russian Patent 50,479, Feb. 28, 1937; Chem. Abs., vol. 31, 1937, p. 8491¹.

Gaseous chlorine is passed over the ore heated to 500° C., together with 1 percent SCl₂ as activator. The chlorinated ore is extracted and the solution subjected to fractional precipitation in the usual manner for separating Cu, Ni, Mg, and Fe chlorides with NaOH.

397. MURAYAMA, AKIRA, AND FUJIMORI, MASAMICHI. [Refining of Nickel.] Japanese Patent 3310, June 9, 1954; Chem. Abs., vol. 49, 1955, p. 6075h.

A nonsulfide-form laterite is fused with coke as a reducing agent and Na₂SO₄, 18–30, CaSO₄, 10–20, and limestone 6–8 percent to recover Ni 92–96 percent as a slag. Quartzite (0–16 percent) and 0.3 percent fluorite can be added in a fusion mixture.

398. SHAKHOV, G. A. [Reaction Between NiSiO₃ and FeS or CaS in the Solid Phase.] Yubilenyi Sbornik Nauk Trudov, Inst. Tsvetnykh Metal i Zolota, No. 9, 1940, pp. 514–523; Khim. Referat. Zhur., vol. 4, No. 5, 1941, p. 80; Chem. Abs., vol. 37, 1943, p. 5678¹.

In the presence of 100 percent excess FeS, reaction with NiSiO₃ in the solid phase begins at approximately 400° C., proceeds slowly at 600° C., is intensive at 700° C., and is complete at 800° C. after 2 hr. and at 1,000° C. after 20 min. With 100 percent excess CaS, NiSiO₃ is completely transformed to NiS in 1 hr. at 1,000° C. The reaction velocity is maximum and the reaction 95 percent complete during the first 20 minutes. In the smelting of oxidized Ni ores, on addition of pyrite, the formation of NiS begins at 400° C. and is completed under 900° C. Addition of gypsum results in a partial reduction of NiSiO₃ and iron oxides at 800°–900° C. and the formation of ferronickel. Thus, the extraction of Ni is higher on addition of pyrite than on addition of gypsum.

399. URAZOV, G. G., AND BOGATSKII, D. P. (N. S. Kurnakov Institute of General Inorganic Chemistry, Academy of Science U. S. S. R., Moscow). [New Trends and Perspectives in the Technology of Complex Iron-Nickel-Cobalt Ores.] Invest. Akad. Nauk. S. S. S. R., Otdel Khim. Nauk., 1948, pp. 194–204 (see Chem. Abs., vol. 40, 1946, pp. 3375¹ and 4632¹; vol. 41, 1947,

pp. 1184i, 3408g, 5367d, and 7343f.); Chem. Abs., vol. 42, 1948, p. 7211g.

Previous work on direct reduction of oxide silicate and of oxide ores by H₂ or CO is recapitulated, and the optimum conditions are summarized. Further treatment of ore following its reduction can be chlorination, leaching, or magnetic separation. Of these three processes, the first two are promising on the basis of laboratory tests. Chlorination of a reduced ore containing Ni 0.6 and Fe 16 percent resulted in complete extraction of Ni in about 3 hr. at 800°–900° C. Although the chlorination process yields the most complete extraction of Ni, Co, and Fe, leaching with 3 percent H₂SO₄ is cheaper and gives extractions of 75 to 95 percent, depending on the ore. Magnetic separation is less satisfactory.

400. VASSERMAN, I. M. [Treating Oxidized Nickel Ores.] Russian Patent 51,092, May 31, 1937; Chem. Abs., vol. 33, 1939, p. 4573¹.

Oxidized Ni ores are melted in the presence of phosphorus-containing additions of the type of phosphorite or apatite to convert Fe and Ni of the ore into phosphides. These are separated from the gangue.

401. WASMUHT, ROLAND. [Behavior of Metallic Oxides and Silicates in a Current of Chlorine.] Ztschr. angew. Chem., vol. 43, 1930, pp. 98–101 and 125–129; Chem. Abs., vol. 24, 1930, p. 3189¹.

Presents a systematic investigation of the behavior of metallic oxides, silicates, and slags in Cl₂ at various temperatures. The effects of C, S, and P upon these reactions are likewise studied.

402. WELCH, A. J. E. (Royal College of Science, London, S. W. 7). Fluorides—Some New Tools for Industry. Sci. Jour. Royal Coll. Sci., vol. 14, 1944, pp. 12–19; Chem. Abs., vol. 40, 1946, p. 1637¹.

A study of the reaction between NaCl, SO₂, and O₂, particularly in the form presented by Johnstone and Dorbyshire (Chem. Abs., vol. 36, 1942, p. 2094¹), led to substitution of NaCl by NaF. Apparently, the use of about 5 percent of sodium fluoride catalyzes the formation of sulfates. Thus nickel sulfate was extracted from garnierite.

403. WESCOTT, E. W. Recovery of Nickel Values From Lateritic Ores. U. S. Patent 2,036,664, Apr. 7, 1936; (see Canadian Patent 353,342, Oct. 1, 1935; Chem. Abs., vol. 29, 1935, p. 7928¹); Chem. Abs., vol. 30, 1936, p. 3393¹.

The ore is treated with gaseous hydrochloric acid and water vapor in such proportions that the Ni is chloridized while the Fe is not.

SMELTING TO FERROALLOYS

404. BAILY, T. F. Production of Nickel and Chrome Steels From Laterite Ores. Trans. Electrochem. Soc., Prep. 88–29, for meeting Oct. 12, 1945, pp. 347–355; Chem. Abs., vol. 40, 1946, p. 523¹; Eng. Index, 1945, p. 737.

Baily's experiments were carried out in an electric arc furnace applying selective reduction of Cuban ores. The basic principle of the experiments is that nickel oxide is more readily reduced than iron oxide and iron oxide more readily reduced than Cr₂O₃. These tests showed that only the nickel oxide, part of the iron oxide, and none of the Cr₂O₃ were reduced. The process offers commercial adaptation where power costs are low and other favorable conditions obtain. The quality of the steel ingots produced from the treated ore competes with that of the best.

405. ———. Reducing Iron Ores Containing Other Metal Oxides. U. S. Patent 2,395,029, Feb. 19, 1946; Chem. Abs., vol. 40, 1946, p. 2432¹.

Ores containing, in addition to iron oxide, the oxides

of the more easily reducible metals Ni and/or Co, as well as less easily reducible oxides, such as those of Cr, Mn, and V, are smelted with only enough reducing agent to reduce the Ni and Co with part of the Fe. A ferronickel or ferrocobalt alloy is formed. The remaining iron and other metals are oxides in a slag. In a second melt the remaining metals are recovered, also as Fe alloys.

406. BANNING, L. H. The Role of the Electric Arc Furnace in Utilizing Some Strategic Offgrade Ores. *Electrochem. Soc. Jour.*, vol. 101, December 1954, pp. 613-621; *Metals Rev.*, vol. 28, No. 3, March 1955, p. 24, 23-C.

The use of a dry-top, arc-resistance electric smelting technique, and smelting-test data are discussed. A relationship between theoretical smelting efficiency and the slag-to-metal ratio is set forth. Tables, graphs, and 10 refs. are included.

407. BANNING, L. H., AND ANABLE, W. E. Preliminary Electric Smelting Research on Philippine Nickeliferous Ores. Bureau of Mines Rept. of Investigations 5129, 1955, 13 pp.

A small shipment of serpentine and laterite from the Surigao area on the Island of Nonoc in the Philippines received by the Bureau of Mines assayed 1.89 and 1.84 percent Ni and 8.47 and 22.8 percent Fe, respectively; after calcining, the serpentine analyzed 2.25 percent Ni and 11.0 percent Fe and the laterite 2.20 percent Ni and 26.9 percent Fe. A local Philippine product, bagasse, was used as reductant in the smelting to ferronickel, always maintaining a dry top on the charge. In the first tests, using a very limited amount of reductant, 38 percent of the Ni was recovered in an alloy of 68.3 percent Ni and 29.9 percent Fe from the calcined serpentine; the alloy from the smelting of the laterite contained 37.4 percent Ni and 61.6 percent Fe. As the supply of original ore was now exhausted below the tonnage needed for further tests, the slag was crushed and resmelted to determine what results might be expected with enough reductant. Over 90 percent of the Ni was recovered in alloys containing 52.1 percent and 48.0 percent Ni, respectively, from the serpentine and laterite. A larger shipment of ore for additional tests seems to be indicated.

408. BUFFALO ELECTRIC FURNACE CORP. Iron and Its Alloys, Nickel, etc. British Patent 355,700, June 27, 1929; *Chem. Abs.*, vol. 26, 1932, p. 2930.

In extracting and refining metals and in manufacturing alloys, a powdered charge (such as Fe, pyrolusite, C, and flux for making ferromanganese) is heated to the fusion point as it is forced through a tube terminating at or near an electric arc (for which the tube may form an electrode). The process is applicable to the reduction of complex Ni ores, recovery of metals from fine dusts, and the production of ferro-silicon, calcium carbide, tungsten, and other heavy metal carbides. Various details of the apparatus and its operation are discussed.

409. CREMER, HERBERT (Bureau of Mines, Albany, Oreg.). Continuous Electric Smelting of Low-Grade Nickel Ores. Bureau of Mines Rept. of Investigations 5021, 1954, 36 pp.; *Chem. Abs.*, vol. 48, 1954, p. 50451.

The most likely domestic sources of Ni are low-grade oxide and silicate deposits, such as the Cle Elum deposit, Kittitas County, Wash., and the Riddle deposit, Douglas County, Oreg. About 40 continuous smelting tests were made on ores from these 2 districts and on Brazilian Ni ore in 2 industrial-type, electric-arc smelting furnaces. The purpose was to produce low-C ferronickel. The method of "dry-top" smelting with hogged-wood waste as reducing agent was the most satisfactory. In this method, a molten pool of slag was developed, and then a 6- to 12-inch layer of charge

was gradually built up over the pool. This floating layer acted as a roof to hold the heat in the furnace and allowed partial reduction of the charge by the action of CO passing up through it.

410. DEMENOV, N. [Science and Industry in the Urals.] *Sovet. Nauk*, No. 7, 1940, pp. 142-144; *Chem. Abs.*, vol. 36, 1942, p. 4786¹.

In the blast-furnace smelting of Cr-Ni ores from Khalilov deposits, it was found that a considerable transfer of Cr into the slag occurred under the conditions of cold working and a highly acid slag. In the blast-furnace smelting of Akkerman's Fe-Ni ores, a new method was developed for extracting more Ni, and the consumption of fuel was reduced by half to two-thirds. At present naturally alloyed steels are obtained with 2 to 2.5 percent Ni. A new method is given for producing large anodes (up to 170 kg.) of high quality from fainstein (an alloy of Ni, Fe, Co, and S).

411. FERRENTE, CORRADO. [The Electrothermic Treatment of Nickeliferous Minerals From Lokrys, Greece.] *Jour. du four électrique*, vol. 60, 1951, pp. 115-117; *Chem. Abs.*, vol. 47, 1953, p. 891; *Metals Rev.*, vol. 25, No. 1, January 1952, p. 22 (8-C).

The average composition of this mineral was Fe 36, Ni 2.38, Co 0.05, Cr 1.88, Mn 0.28, SiO₂ 16.98, Al₂O₃ 17.41, CaO+MgO traces, Ti 0.66, S 0.12, and volatiles 6.35 percent. By using a matte process, it was possible to produce a 40-percent Ni matte with 0.8 percent Ni in the slag, but this process had to be abandoned because of lack of equipment.

Using a 12,000-kv. a. furnace, blowing in a Bessemer converter, and refining in a Heroult furnace, a product was obtained assaying 6.5-7.0 percent Ni, with C 3-3.2, Cr 0.3-0.5, and S 0.25-0.3 percent. The high S and Cr content necessitated further experimental work. Finally, a ferronickel was produced, averaging 22.28 percent Ni, with some melts assaying 40 percent Ni. The technique involved a charge of mineral 1,000, lime 50, metallurgical coke 20, and anthracite 40 parts. The slag, carrying off the Cr, assayed as high as 46 percent ferrous oxide.

412. FUKABORI, SAICHI (assigned to Kanto Special Steel Manufg. Co.). [Ferronickel From Serpentine.] Japanese Patent 1815, Apr. 7, 1954; *Chem. Abs.*, vol. 49, 1955, p. 143i.

Serpentines of low Ni content (Ni 0.18-0.29 percent) and rock phosphate are mixed in the proportion: P₂O₅:CaO:SiO₂:MgO of 1:5-9:2-6:1-2 moles, and heated in a C-coated furnace at 1,350° C. to recover the Ni in the serpentines as Fe-Ni-P and phosphate slag, which can be used as a fertilizer. The molten Fe-Ni-P is refined by blowing in O₂, air, or wet air to obtain Fe-Ni.

413. HUNDHAUSEN, R. J., McWILLIAMS, J. R., AND BANNING, L. H. Preliminary Investigation of the Red Flats Nickel Deposit, Curry County, Oreg. Bureau of Mines Rept. of Investigations 5072, 1954, 19 pp.; *Chem. Abs.*, vol. 48, 1954, p. 13571f.

The deposit contains areas of Ni-rich brick-red soil, termed nickeliferous laterite, and an underlying zone of weathered nickeliferous serpentine. A 15-ton sample of ore, as received, contained 31 percent moisture. After drying to 18 percent moisture and crushing to minus-½-inch, the ore analyzed Ni 0.74 and Fe 28.2 percent. A charge of ore (100) and wood chips (17) lb. was smelted without a flux in a round, open-top, pit-type, 3-phase ESA furnace. Overall recovery figures indicated that 82.2 percent of the Ni and 12.8 percent of the Fe charged were recovered in ferronickel products analyzing 9.29-14 percent Ni. The average power and graphite consumption was 1.073 kw.-hr. and 10.52 lb. of graphite, respectively, per ton of dry ore smelted.

414. KIKUTI, HIDEYUKI. Extracting Metals. British Patent 500,722, Feb. 13, 1939; Chem. Abs., vol. 33, 1939, p. 5299¹.

Ores are reduced by subjecting them to the action of currents having a frequency above 100,000 cycles per second in an electrode furnace, the applied voltage being above 1,000 volts. The ore, mixed with small quantities of reducing agents, with or without fluxes, is in the form of small granules forming an electrically discontinuous conductive mixture. To provide a good, discontinuous conductor, conductive materials (for example, graphite, charcoal, or metals) or nonconductors (such as coal, lignite, oil shale, or wood chips) may be added; piezoelectric materials such as quartz may be used. Ores may be selectively reduced. Examples are given of the reduction of garnierite to produce ferronickel containing Fe 80 and Ni 18 percent; of Co ore for the production of ferrocobalt containing Fe 77, Co 22, C 0.3, P 0.02, Si 0.09 percent, and As and S, traces.

415. KIRSEBOM, G. N., and CALLOY, LTD. Extracting Metals. British Patent 446,502, Apr. 23, 1946; Chem. Abs., vol. 30, 1936, p. 6693⁵.

Metalliferous materials that are solid at the temperature of molten Mg and contain metals, the oxides of which have a heat of formation less than that of MgO, are heated as pieces or lumps greater than 1 mm. diameter with Mg in a closed vessel at a temperature sufficient to melt the Mg. The dross obtained in the reaction may be again reduced to Mg in an Al bath and the Mg recovered by distillation. Ca, Ba, or Sn or alloys of these metals with Mg may be produced by using the oxides as starting materials or an alkaline earth-Si-Mg alloy may be formed by use of the silicate. The oxide dross produced by the process of British Patent 397,844 (Chem. Abs., vol. 28, 1934, p. 1012⁶) may be treated by the process, for example, a dross consisting of BeO, Al₂O₃, and Al, formed by adding beryl to molten Al, may be introduced into molten Mg to form an Al-Be-Mg alloy. Alternatively, the dross may be subjected to an oxidizing roast prior to treatment with Mg, when a Mg-Be alloy is produced from which the Mg may be removed by distillation. The process may also be applied to the extraction of Sn, Cr, V, U, Ni, and the rare-earth metals.

416. LIGHTY, L. J. (assigned to Quebec Metallurgical Industries, Ltd.). Nickel From Nickel Silicate Ore. U. S. Patent 2,573,153, Oct. 10, 1951; Chem. Abs., vol. 46, 1952, p. 3940b.

Low- or medium-grade nickel silicate ore containing 0.75–3.0 percent Ni and about 3 times as much Fe is smelted with Alsifer (Si 66.5, Al 8, and Fe 25 percent) or other reducing agent in an amount determined by the formula, $100 \frac{x}{3y}$, where "x" is the weight of Ni in the ore, and "y" is a number between 30 and 60 representing the percentage of Ni desired in the Fe-Ni alloy produced. A correction is applied to the formula if the reductant composition differs. Lime is added as a flux, and the mixture is heated at 1,500° C. The molten Fe-Ni alloy settles to the bottom. Cu and Co as impurities are also reduced.

417. LINDSLEY, THAYER, and LIGHTY, L. J. (assigned to Quebec Metallurgical Industries, Ltd.). Reduction of Metal Oxides. U. S. Patent 2,653,867, Sept. 29, 1953; Chem. Abs., vol. 48, 1954, p. 535b.

A high-grade ore, such as magnetite, is smelted in a mixture of charcoal and ferrosilicon or aluminum ferrosilicon at a temperature not substantially greater than the melting point of the reduced metal. The proportion of charcoal is calculated to combine with 45–85 percent of the given weight of the oxide O and the ferrosilicon ingredient calculated to combine with the remainder. The use of Si, Ca, and Mg instead of the ferrosilicon is mentioned. The method is applicable

to the smelting of various oxide ores, including Fe, Cr, Mo, W, V, Ni, and Co.

418. LYON, D. A., KEENEY, R. M., and CULLEN, J. F. Ferronickel. The Electric Furnace in Metallurgical Work. Bureau of Mines Bull. 77, 1914, pp. 151–154.

Ferronickel is ordinarily made by incorporating metallic Ni in steel. Three projects are cited in which it was smelted directly from ores. In an electric furnace at Sault Ste. Marie, several runs were made on the reduction of roasted pyrrhotite containing Ni, eventually producing ferronickel. Owing to the low percentage of Ni in the ore, and a low Ni product, there was difficulty in marketing, and the ferronickel was not pure enough or high enough grade for steel manufacture.

A plant was erected at Webster, Jackson County, N. C., where experiments were conducted on the reduction of garnierite in the electric furnace with coke as a reducing agent. The product contained 10–30 percent Ni, 20–30 percent Si, 40–50 percent Fe, 5–10 percent Al, and 3–5 percent Cr. The power was very expensive, and the plant no longer operates. In 1903, at the works of the Société Anonyme Electrometallurgique Procédés Paul Girod, a product was made containing 30 percent Ni and 47.20 percent Si. Experiments to make a ferronickel were tried, making an alloy of Ni 41.50 and Fe 51.6 percent. Power consumption and apparatus used are detailed.

419. MIKHAILOV, V. V., and SIGOV, A. A. [Blast-Furnace Smelting of a Mixture of Nickel Ores of Ackermann Deposits With Vysokogorsk Martites.] Ural-Met., vol. 9, No. 11/12, 1940, pp. 14–19; Chem. Zentralb., vol. II, 1941, pp. 1192–1193; Chem. Abs., vol. 38, 1944, p. 1713⁷.

The smelting of crude pulverulent Ni-Fe ore of Ackermann deposits to Ni-containing pig iron in coke blast furnaces confirmed the possibility of further development of this method. It would be necessary, for the increase of Ni content in pig iron (6–10 percent) to use agglomerated ore which would be sufficiently fluid when lime is added. In a mixture of Ackermann deposit ores with Vysokogorsk ores, the slag is thinly fluid and has the property of desulfurization.

420. MUKOYAMA, MIKIO. [Treatment for Nickel-Containing Iron Ore.] Japanese Patent 2460, June 2, 1953 (see Chem. Abs., vol. 47, 1953, p. 5344b); Chem. Abs., vol. 48, 1954, p. 8159c.

421. PAWEI, G. W. Ferronickel. U. S. Patent 2,468,103, Apr. 26, 1949; Chem. Abs., vol. 43, 1949, p. 5726h.

The first step in beneficiating low-grade Ni ores, such as garnierites, is a classification into fines, containing 40 percent of the original Fe and Ni present, and coarse fractions. The former are smelted directly to obtain ferronickel, and the latter are relatively easily leached with about half the usual amount of HCl to recover all but 10 percent of the Ni, which is lost with the discarded 50 percent of the ore.

422. RASMUSSEN, R. T. C. Electric Smelting of Bureau of Mines Seeks Utilization of Northwest Ores. Jour. Metals, vol. 4, No. 12, December 1952, pp. 1273–1279; Eng. Index, 1953, p. 420.

Research facilities comprise batch-type arc-melting furnaces and pilot-plant smelter with two open-top, pit-type furnaces for continuous smelting tests. Production of ferronickel from nickel silicates and other activities are mentioned.

423. RAVITZ, S. F. Electric Smelting of Low-Grade Nickel Ores. Bureau of Mines Rept. of Investigations 4122, 1947, 39 pp.; Eng. Index, 1945, p. 580; Chem. Abs., vol. 44, 1950, p. 8795h.

Supplementing a report indexed in Engineering Index, 1945, p. 580, from Trans. AIME, vol. 159, more

work was done on the Cle Elum and Blewitt Pass ores and on ore from a surface deposit near Riddle, Oreg. The results of ore dressing, leaching, and electric smelting are related. In the electric smelting, starting with 3 Fe ores bearing 1-2 percent Ni, a partial reduction in an electric arc furnace produced a ferroalloy assaying 25-30 percent Ni, suitable for preparation of Ni alloy steels. Oxidation of this alloy with an Fe or Ni-Fe ore yields a not more than 75 percent Ni ferroalloy. Slag from the partial reduction of one ore contained Fe 50 and Cr 2 percent; on smelting this with an excess of C, the metals were reduced to cast iron containing the Cr. With close control of the C, 50 percent of the Cr was recovered as a low-C, 2-percent Cr steel.

424. RAVITZ, S. F., MILLER, VIRGIL, AND PETERMANN, F. B. Electric Smelting of Cle Elum-Blewitt Pass Nickeliferous Iron Ore. *Trans. AIME, Ferroalloy vol. Reduction and Refining of Nonferrous Metals*, vol. 159, 1944, pp. 442-445; pres. at ann. meeting AIME, New York, February 1944; *Eng. Index*, 1945, p. 580.

425. SOCIÉTÉ D'ÉLECTROCHIMIE, D'ÉLECTROMÉTALLURGIE ET DES ACIÉRIES ÉLECTRIQUES D'UGINE. Extraction of Nickel From Low-Grade Ores. *British Patent* 713,713, Aug. 18, 1954; *Chem. Abs.*, vol. 49, 1955, p. 2285g.

Ni is extracted from low-grade ores as an Fe-Ni alloy by mixing successive charges of molten ore with molten Fe and periodically withdrawing a part of the metal. Exothermic heat from oxidation of added Si or Al compensates for heat losses. Formation of CO from C addition causes bubbling. Treatment of ore containing NiO 1.5, FeO 35, and SiO₂ 35 percent with Fe and Fe-Si in a converter produces a slag containing 0.20 percent Ni and after processing gives a 30-percent Ni alloy.

426. TAKAKUWA, TOKUICHI. [Low-Carbon Nickel Steel.] *Japanese Patent* 1814, Apr. 7, 1954; *Chem. Abs.*, vol. 49, 1955, p. 825f.

Powdered Fe ore (-100-mesh) containing Fe 49, Ni 0.8, Mn 1.0, SiO₂ 13, and Cr 3.5 percent is mixed with 5.2 percent by weight of powdered coke and 25 percent by weight of water and is heated in an electric furnace to give a Ni steel containing C 0.031, Ni 4.27, P 0.004, and S 0.09 percent.

427. ZOLDOK, S. W. Cle Elum Iron-Nickel Deposits, Kittitas County, Wash. *Bureau of Mines Rept. of Investigations* 4189, 1948, 8 pp.

The Cle Elum nickeliferous Fe deposits occur in a serpentine formation extending about 20 miles along the Cle Elum River in Kittitas County, Wash. The principal ore minerals are magnetite, hematite, and limonite, which occur intermixed and are intimately associated with serpentine, olivine, and rock decomposition products. The Bureau has made an extensive metallurgical investigation of the Cle Elum Fe-Ni ores, resulting in an electric smelting process and ending in a high-grade Ni-Fe alloy. The Fe can be recovered as low-Cr steel, reported in *Bureau of Mines Rept. of Investigations* 4122, by Ravitz, S. F.

PYRO TREATMENTS; NON- OXIDIZED ORES AND SALTS REDUCTION TO METAL OR METAL- LURGICAL PRODUCT

428. ASHCROFT, E. A. Treating Nickel and Copper Ores, etc. *U. S. Patent* 1,851,885, Mar. 29, 1932 (*see British Patent* 338,556; *Chem. Abs.*, vol. 25, 1931, p. 2406); *Chem. Abs.*, vol. 26, 1932, p. 2955.

429. BEIDLER, E. A. (assigned to Crowley-Republic Steel Corp.). Low-Temperature Reduction of Nickel Chloride. *U. S. Patent* 2,642,356, June 16, 1953; *Chem. Abs.*, vol. 47, 1953, p. 7994h.

The reaction of solid dry NiCl₂ with dry H₂ will not proceed to any substantial extent in the temperature range 475°-650° F. In the procedure described in the present patent, metallic nickel is introduced as a reaction-initiating catalyst.

430. ——— (assigned to Crowley-Republic Steel Corp.). Reduction of Cobalt Chloride to Cobalt Powder. *U. S. Patent* 2,642,357, June 16, 1953; *Chem. Abs.*, vol. 47, 1953, p. 7994d.

By using finely divided Co metal as a catalyst with cobalt chloride, the temperature of the initial reduction is lowered from 690° to 510° F.

431. BERDNIKOV, A. E., AND ZAKHAROV, M. I. [Composition of the Gases From the Reductive Smelting of Nickel.] *Tsvetnye Metal*, vol. 13, No. 4, 1938, pp. 65-69; *Chem. Zentralb.*, vol. I, 1939, pp. 1051-1052 (*see Chem. Abs.*, vol. 33, 1939, p. 2857⁷); *Chem. Abs.*, vol. 35, 1941, p. 2099².

A water-jacketed furnace provided with a rotating mechanism operated at 10-25 r. p. m. was tested by the use of 30-35 kg. lime and 8-12 kg. gypsum per 100 kg. Ni ore at an air consumption of 24 to 25 m.³ per minute. The reducing action took place throughout the furnace but was especially vigorous about 0.5-1 m. above the tuyères. The waste gas (temperature 90°-110° C.) was usually O₂-free and contained 17-19 percent CO₂ and 2-4 percent CO (at most 8-10 percent); with normal furnace operation the CO₂/CO ratio is 2. Under the tuyères the temperature was 1,300°-1,400° C. and the CO content of the gas 40 percent.

432. KISSOCK, ALAN. Recovery of Metals From Nickeliferous Iron Ores. *U. S. Patent* 2,197,185, Apr. 16, 1940; *British Abs.*, 1946, p. B-1-96; *Chem. Abs.*, vol. 34, 1940, p. 5406².

An ore containing Fe and Ni is treated at temperatures of 425°-650° C., under reducing conditions, and in the absence of free O₂ and with enough available S to convert at least the major portion of the Ni to sulfides or to compounds with lower O content than the sulfate. The reduced ore is cooled below 100° C. in the absence of air and subjected to oxidation as by an H₂O₂ solution or persulfate solution to convert the Ni to a water-soluble compound, which is then leached with water.

433. KOMURO, SHIZUO. [Roasting of Nickel Arsenide or Thioarsenide Ore.] *Japanese Patent* 109,793, Feb. 28, 1935; *Chem. Abs.*, vol. 29, 1935, p. 4727¹.

The roasting is effected at 250°-500° C. with rapid agitation or at 500°-700° C. with slow agitation, in a current of air under a pressure of more than 5 mm. of water.

434. KUZELL, C. R. (assigned to Phelps Dodge Corp.). Treatment of Ores Containing Sulfides of Iron, Copper, and Nickel. *U. S. Patent* 2,111,789, Mar. 22, 1938; *Chem. Abs.*, vol. 32, 1938, p. 3747².

The ore is subjected to intensive oxidation to form a molten product, largely Fe₂O₃, which is selectively reduced by a gas or finely divided solid to form separable Cu, Ni, and Fe products.

435. OGORZALY, H. J. (assigned to Standard Oil Development Co.). Reduced Metal Dust. *U. S. Patent* 2,540,593, Feb. 6, 1951; *Chem. Abs.*, vol. 45, 1951, p. 3789g.

A continuous method of melting finely divided particles in a controlled atmosphere is presented. Finely divided sponge-iron particles are produced by reduction of an Fe ore at a temperature (1,050° F.) below the fusion point of the metal. The reduced sponge Fe is treated in suspension in a high temperature (2,900°

F.) gaseous mixture so that it is fused in a relatively short period of time. The molten droplets are collected and separated from the gasiform material. This gas may consist of H_2 , H_2O , CO , and CO_2 and is so proportioned that it is nonoxidizing or carbonizing to the metal particles. The process may be applied to CuS - NiS ores in Na_2S , to effect a separation of molten gangue materials from the metal-bearing portion of the melt, and of the NiS and CuS portions of the melt from each other.

436. QUENEAU, P. E., SPROULE, W. K., AND ILLIS, ALEXANDER (assigned to International Nickel Co.). High-Grade Iron Oxide From Ores Rich in Nickeliferous Pyrrhotite. U. S. Patent 2,556,215, June 12, 1951; Chem. Abs., vol. 45, 1951, p. 8434c.

The finely divided ore is subjected to a series of flotation and desliming operations, with or without magnetic separation. A clean, nickeliferous pyrrhotite concentrate is produced, and one or more high-grade concentrates containing the Cu, precious metals, and the rest of the Ni. The nickeliferous pyrrhotite is roasted, preferably in a furnace of the injection-suspension or fluid-bed type to obtain a low-sulfur calcine. This is selectively reduced so that all of the Ni is substantially soluble in an ammoniacal leaching solution. Fe, however, should be substantially insoluble in the latter. The residue contains approximately 95 percent of finely divided ferric oxide.

REDUCTION TO MATTE OR SPEISS

437. BARTHEL, JOACHIM [The Recovery of Nickel From Low-Grade Oxide Ores.] Bergakademie, Freiberg, Forsch., B. Hüttenw.—Met., No. 3, 1952, pp. 17–26 (pub. 1953); Chem. Abs., vol. 48, 1954, p. 3875e.

A process is proposed for utilizing low-grade oxide ores of Ni. The ore is subjected to sulfide smelting, by the addition of gypsum and coal, in a continuous reverberatory furnace operated at $1,300^{\circ}$ – $1,350^{\circ}$ C. The ore, reduced to a 10-mm. particle size, requires no briquetting. The use of high-quality coke is unnecessary, and low-grade fuels can be used. Waste-heat boilers use the stack gases. The furnace capacity is 1.5 to 2 tons of ore per m^2 per day.

438. BENITEZ, F. Flash Smelting at Harjavalta's Smelter of Outokumpo Oy, Finland. Eng. and Min. Jour., vol. 154, No. 10, 1953, pp. 78–80; Metals Rev., vol. 28, No. 7, July 1955, p. 31 (89c).

439. BRYK, P. Flash Smelting at Outokumpo Oy. British Nonferrous Metals Research Assoc., Misc. Publ. 435, December 1951 (translation); Canadian Min. and Met. Bull., vol. 48, No. 517, May 1955, pp. 292–300; Metals Rev., vol. 28, No. 7, July 1955, p. 31 (89c).

In a flash smelting process at the Harjavalta smelter, Outokumpo Oy, since oxygen is not available, the combustion air is preheated by heat exchange with exit gases. Pilot-plant studies were initiated in February 1947, and semiautogenous operation was begun on a large scale in 1949.

440. DIEV, N. P. AND TSEFT, A. L. [Water-Jacket Smelting With the Use of Oxygen-Enriched Air.] Tsvetnye Metal, 1940, No. 2, pp. 64–67; Chem. Abs., vol. 35, 1941, p. 627.

The authors discuss the advantages of the use of air enriched in O_2 (30–80 percent O_2) in pyritic and semipyrritic smelting of Cu, in smelting of Ni from sulfide ores, and in reduction smelting of Zn. The main advantages are: Increase in the capacity of the furnaces (furnace output); higher temperatures obtainable; exhaust gas richer in CO , as a byproduct; and decreased cost of smelter construction. The authors urge experi-

mental work on a semicommercial scale to obtain accurate experimental data on the technical and economic advantages of the use of O_2 -enriched air.

441. GORDON, J. R., AND OTHERS (assigned to International Nickel Co., Inc.). Autogenous Smelting of Sulfides. U. S. Patent 2,668,107, Feb. 2, 1954; Chem. Abs., vol. 48, 1954, p. 5777h.

Improvements in the production of matte rich in Ni and/or Cu, directly from Ni and/or Cu concentrates with recovery of SO_2 , consist in smelting above $2,000^{\circ}$ F. a mixture of high-grade sulfide concentrate containing 75–95 percent chalcopryrite and less than 0.5 percent free moisture with a siliceous flux and an oxidizing gas containing 65–98 percent O_2 to obtain a high-Cu matte, a high-Cu slag, and SO_2 suitable for direct liquefaction by compression. A low-grade S concentrate containing 80–95 percent pyrrhotite and less than 0.5 percent free moisture is smelted with a siliceous flux and an oxidizing gas containing 65–98 percent O_2 to oxidize a major portion of the concentrate and produce a low-grade matte rich in iron sulfide and low in Ni and/or Cu and a low-grade slag. The molten, low-grade slag is showered as molten droplets on the high-grade molten siliceous slag to pass through it and remove the bulk of the Cu and secure an enriched Cu matte. At one point, the high-grade Cu matte is tapped before smelting of the low-grade concentrate was completed. At another point, impoverished slag is tapped in countercurrent flow to the matte and SO_2 is recovered. The high-grade S concentrate used can contain 10–75 percent pentlandite (or pentlandite and chalcopryrite) to secure a high-grade Ni matte and a high-grade Ni-rich siliceous slag.

442. GORDON, J. R., NORMAN, H. C., QUENEAU, P. E., SPROULE, W. K. AND YOUNG, C. E. (assigned to International Nickel Co. of Canada, Ltd.). [Recovery of Nickel and Copper From Ores.] German Patent 840,441, June 9, 1952 (*Cl. 40a 43a*); British Patent 672,418, May 21, 1952, Chem. Abs., vol. 46, 1952, p. 9051b; Chem. Abs., vol. 49, 1955, No. 4, p. 2285g; and vol. 46, 1952, p. 9051b.

The concentrated sulfides are flash-smelted to yield a matte rich in Ni and Cu. The overlying slag contains appreciable quantities of Cu and Ni. To recover this, finely divided iron sulfide is flash-smelted with a flux to oxidize and slag part of the sulfide. The remainder is converted to molten drops of iron sulfide, which are made to fall through the slag and carry the Ni and Cu into the matte below. This method is particularly suited to pyrrhotite ores because they can be separated into 2 concentrates, 1 rich in NiS and CuS and the other rich in pyrrhotite.

443. ———. Flash Smelting. Canadian Patent 503,446, June 1, 1954; U. S. Patent 2,668,107, Feb. 2, 1954; Canadian Min. Met. Bull., vol. 48, No. 517, May 1955; Metals Rev., vol. 28, No. 7, July 1955, p. 31 (89c).

444. GRONNINGSÆTER, A. M. (assigned to Falconbridge Nickel Mines, Ltd.). Reducer-Mixer for Nickel-Copper Smelting Assembly. U. S. Patent 2,426,607, Sept. 2, 1947; Chem. Abs., vol. 41, 1947, p. 7371i.

A continuous-operation reducer-mixer to be used in connection with the conventional blast or reverberatory furnace is described. Its advantages are economy of fuel and labor, as well as substantial increase of recovered Co when smelting nickel sulfide ore. Structural and operational details are given.

445. INTERNATIONAL NICKEL CO. STAFF. The Oxygen Flash-Smelting Process of the International Nickel Co. Canadian Min. and Met. Bull. 58, No. 517, May 1955, pp. 292–300; Metals Rev., vol. 28, No. 7, July 1955, p. 31 (89c); Chem. Abs., vol. 49, 1955, p. 8757g.

A process, somewhat similar to the one in use at

Outokumpo Oy, Finland, Harjavalta smelter, has been developed for the flash smelting of copper-nickel sulfides. Slag losses are lower than in conventional reverberatory practice. In this location, low cost oxygen is available. Diagrams and illustrations are included with 17 refer.

446. LINDBLAD, A. R. [Cobalt From Copper Sulfide Ores.] Swedish Patent 84,906, Dec. 3, 1935; Chem. Abs., vol. 30, 1936, p. 6314².

Co-containing copper sulfide ores are bessemerized with a silicate or silica to obtain Co in the slag, which is then reduced in the presence of As and S in a melt. The Co-speiss and the crude ores separate from each other by settling to the bottom. The Co-speiss is oxidized in a Bessemer converter to drive off As, after which it is worked up by reduction or acid treatments.

447. LONGENECKER, L. S. Reverberatory Furnaces—Possible Improvements for the Smelting of Copper and Nickel. Canadian Min. Jour., vol. 65, 1944, pp. 370-374; Chem. Abs., vol. 38, 1944, p. 4223².

448. NORDDEUTSCHE AFFINERIE. Matte and Speiss Collecting Processes. British Patent 369,120, Sept. 9, 1930; Chem. Abs., vol. 27, 1933, p. 2124.

Ores or metallurgical products containing Ni and Co are subjected to a concentrating process to separate Cu, Fe, Pb, and noble metals as a matte and to form a concentrated speiss containing Ni, Co, As, and Sb. Concentration of crude speiss is effected by fusion with S, while crude matte may be fused with products containing As to separate Ni and Co as a concentrated speiss.

449. NORMAN, T. E. Flash Smelting. Eng. and Min. Jour., vol. 137 (10-11), 1936, pp. 499-502 and 562-567; Canadian Min. Met. Bull., vol. 48, No. 507, May 1955, pp. 292-300; Metals Rev., vol. 28, No. 7, July 1955, p. 31 (89c).

Oxygen or oxygen-enriched air is used in the autogenous flash smelting of Cu and Cu-Ni concentrates.

450. NOVIKOV, D. G. [Shaft Smelting of Copper and Nickel Ores.] Tsvetnye Metal, No. 9, 1940, pp. 58-67; Khim. Referat. Zhur., vol. 4, No. 4, 1941, pp. 91-92; Chem. Abs., vol. 37, 1943, p. 4995².

Discusses the mechanism of pyrite smelting, the main chemical reactions, the role of fuel, and the peculiarities of semipyrith smelting of Cu. The methods proposed to increase the capacity of the Ural metallurgical plants consist chiefly of sifting out the fine grains of the charge and breaking the coarse grains to 10-110 mm. The size of the flux lumps must be 20-110 mm. The size of coke lumps must be 20-50 mm. to give a porous mixture and rich mattes. The components must be mixed carefully before charging. In smelting Ni ores, it is proposed to replace gypsum by pyrite and a part of the CaCO₃ by iron-containing flux, to use return slag from the converter, and to replace a part of the coke by anthracite.

451. ROBIETTE, A. G. E. Electric Smelting of Non-ferrous Metals. Metal Ind., vol. 83, No. 9, Aug. 28, 1953, pp. 161-165; Eng. Index, 1953, p. 420.

Discusses electric furnaces and processes employed in smelting sulfide concentrates and ores of both Cu and Ni for production of matte and for smelting of Sn, Zn, and oxidized Ni ores.

452. SHIZUO, KOMURO. [Concentrating Nickel Speiss.] Japanese Patent 110,300, Apr. 12, 1935; Chem. Abs., vol. 29, 1935, p. 7927⁵.

Melted Ni speiss is mixed with silica, limestone, soda ash, sodium sulfide, and a fuel and heated in a blast; a speiss rich in Ni is obtained.

453. SIMCOX, I. J., AND PEEK, R. L. (assigned to International Nickel Co. of Canada, Ltd.). Smelting

Matte-Forming Ores. U. S. Patent 2,035,016, Mar. 24, 1936; Chem. Abs., vol. 30, 1936, p. 2903⁸.

A charge of an ore such as a Cu-Ni concentrate is subjected to a smelting temperature in a reverberatory furnace to produce a matte and a covering layer of slag, which are then passed to an agitation zone and subjected to violent agitation induced by injecting a substantially inert gaseous medium such as steam into the underlying body of matte, and the materials are then passed to a settling zone. Describes apparatus.

454. SMAILL, A. E. Extraction of Metals From Ores. Canadian Patent 289,214, Apr. 30, 1929; Chem. Abs., vol. 23, 1929, p. 3201⁷.

Sulfide ores containing Fe, Ni, and Cu, as well as smaller percentages of precious metals, smelted with an alkaline flux under reducing conditions produce a self-disintegrating matte of metal sulfide containing alkali. The matte is disintegrated by exposure to a moist atmosphere. An alkali-containing compound is added to the disintegrated matte, the mixture is roasted at 600° C. and leached (weak acids, brine, or solutions of ammonia compounds may be used as solvents if required, but hot water will usually dissolve the sulfates) to remove soluble constituents, and the leached residue is subjected to gravity separation to concentrate the precious metal values.

455. SMIRNOV, V. I. [The Efficiency of Blast Furnaces in the Smelting of Copper and Copper-Nickel Ores.] Tsvetnye Metal, vol. 13, No. 10, 1938, pp. 51-60; Chem. Zentralb., vol. I, 1939, p. 3950; Chem. Abs., vol. 34, 1940, p. 7806⁹.

The relation between the mineralogical composition of the slag and of the charge was studied, as was also the influence of air supply on the combustion of fuel and of the sulfides, with special attention to the behavior of the sulfide ores of the Urals.

456. STANLEY, R. C. (Annual Address to Shareholders, International Nickel Co. of Canada, April 1948.) Flash Smelting. Canadian Min. Met. Bull., vol. 48, No. 517, May 1955, pp. 292-300; Metals Rev., vol. 28, No. 7, July 1955, p. 31 (89c).

The development of autogenous smelting at Copper Cliff, Canada, is discussed.

457. TAKEI, TAKESHI, TAKAKUWA, TOKUICHI, AND YOSHIDA, KATSUMI. [An Experiment in Concentrating Nickel by the Matte-Making Method.] Jour. Electrochem. Assoc., Japan, vol. 15, 1947, pp. 13-16; Chem. Abs., vol. 44, 1950, p. 9832a.

Nickel ores (2.6-8.4 percent) were treated with CaSO₄, SiO₂, and C by heating electrically to make matte of NiS and remove Fe as a component of the slag. In methods with the ores as the resistance and methods with an arc furnace for steelmaking, it was difficult to separate the matte from the slag, while the method with Gillaut's electric furnace increased the amount of Ni in the matte by 3-4 times that in the raw ore with a yield of 80 percent Ni.

PYRO TREATMENT OF MATTE OR SPEISS

458. ANAZAWA, KENJI, AND YAMAGUCHI, TAKEJI (assigned to Furukawa Rika Kenkyujo). [Separation of Nickel or Cobalt From Nickel or Cobalt Smelt.] Japanese Patent 172,114, Jan. 9, 1946; Chem. Abs., vol. 43, 1949, p. 6965b.

Unoxidized, partly oxidized, or mixed Ni and Co smelt is melted at 700°-1,000° C. with a mixture of Na₂O 15-45, CaO 0-13, and SiO₂ 55-78 percent to separate Ni or Co.

459. BADISCHE ANILIN-UND SODA-FABRIK (I. G. Farbenindustrie, A. G.). Recovery of Nickel From Nickel-

Copper Matte. British Patent 698,162, Oct. 7, 1953; Chem. Abs., vol. 48, 1954, p. 6365d.

Matte is blown in a converter to 20 percent S or less, heated to permit grain growth and separation into metallic and sulfidic phases, finely ground, and separated magnetically into magnetic, predominantly metallic, and nonmagnetic predominantly sulfidic. In an example, matte containing 54 percent Ni, 26 percent Cu, and 20 percent S is heated for 72 hr. at 500° C., pulverized and magnetically separated. The magnetic fraction contains 71 percent Ni and 28 percent Cu. Leaching with 20 percent H₂SO₄ at 90° C. dissolves 95 percent Ni and 10 percent Cu. The liquor is treated with additional magnetic metallic fraction to precipitate Cu. The C-free solution is worked up into NiSO₄ crystals or electrolyzed to recover Ni, in which case the H₂SO₄ can be recycled. The leach residue is freed from Ni by repeated leaching with acid until it contains only metallic Cu and a small amount of S, as well as Au and elements of the Pt group. It is then treated for electrolytic recovery of the Cu.

460. BADISCHE ANILIN-UND SODA-FABRIK (assigned to I. G. Farbenindustrie, A. G. "In Auflösung.") Processing of Copper Mattes. British Patent 710,827, June 16, 1954; Chem. Abs., vol. 48, 1954, p. 13607a.

Fe-containing Cu-Ni and Cu-Co mattes are adjusted to a controlled S content by roasting or by the addition of Fe or Cu to combine with the desired amount of S. They are then fused and cooled at about 5° C. per hr. to give metallic Ni-Fe particles, CuS, and larger-than-100-micron FeS. The mixture is comminuted to a grain size of about 150 microns, Ni-Fe is separated magnetically, and CuS is separated from FeS by flotation. The Ni-Fe portion is suitable for carbonyl refinement or for production of ferronickel.

461. BOGATSKII, D. P. [Conversion of Nickel Matte.] Russian Patent 59,276, Feb. 28, 1941; Chem. Abs., vol. 33, 1945, p. 900².

The matte is blown with H₂, CO, CH₄, or other active reducing agents.

462. BOGITCH, B. [The Roasting of Sulfides: Nickel Mattes in Particular.] Compt. rend., vol. 196, 1933, pp. 782-784; Chem. Abs., vol. 27, 1933, p. 4033.

The S in a Ni matte that originally contained 22.4 percent S was reduced to 18.7 percent in 8 hr. at 700° C.; to 13.6 percent in 16 hr. at 825° C.; to 6.1 percent in 24 hr. at 1,025° C.; to 3.6 percent in 32 hr. at 1,110° C.; and to 1.4, 0.32, and 0.02 percent in 35, 38, and 40 hr., respectively, at 1,200° C. In the commercial process, most of the S is eliminated at low temperatures, with a brief exposure at a higher temperature.

463. BORCH, N. S. (assigned to F. L. Smidt & Co.). Desulfurization of Nickel Matte. Canadian Patent 396,238, Oct. 29, 1941; U. S. Patent 2,157,254, May 9, 1939; Chem. Abs., vol. 33, 1939, p. 6217⁴; Chem. Abs., vol. 35, 1941, p. 5084⁷.

A mixture of roasted and unroasted Ni matte relatively low in S is heated at about 1,000° C. in the presence of an excess of O₂ to decrease the S content, and the temperature is increased to at least 1,100° C. to eliminate most of the remaining S, the operation being carried on continuously. Describes the apparatus.

464. ———. Roasting Nickel Mattes. British Patent 488,568, July 8, 1938; Chem. Abs., vol. 33, 1939, p. 109³; British Chem. Abs., vol. 33, 1939, p. B-60.

In roasting Ni matte in a rotary kiln, the unroasted matte is mixed with the roasted matte to lower the S content, for example, to about 8 percent, so as to reduce the risk of partial melting. Roasting is effected at about 1,000° C. in the presence of a substantial excess of O₂. The roasted matte may be heated to

1,100°–1,300° C. to remove residual S, the heating being effected in the presence of only a small excess of O₂. The two operations may be performed in a single rotary kiln, the material to be roasted and the combustion gases being led through countercurrent to each other. The gases entering the kiln may contain only a small excess of air admitted at one or more points in the kiln shell.

465. BORCHERS, HEINZ, AND HERMANN, GERHARD. [Oxidation of Metallic Sulfides by Roasting.] Bol. minerio Soc. nacl. miner (Santiago, Chile), No. 583, 1948, pp. 650-657; Chem. Abs., vol. 48, 1954, p. 516d.

Sulfo salts were roasted at temperatures between 600° and 1,000° C. Eight graphs showing changes in composition with variations in temperature and time of roasting are given. Changes in density of 12 samples before and after roasting are tabulated.

466. DOWNIE, C. C. Researches on Nickel Matte. Min. Jour. (London), vol. 238, No. 6072, Jan. 4, 1942, p. 12-B; Eng. Index, 1952, p. 676.

In smelting Ni ores in a blast furnace followed by refining of matte produced in a converter, the work proceeds in a more or less direct manner as long as magnesia, silica, and iron oxide contents are within limits for easy fluxing. The processes used are described, with mention of adaptation of the oxalic acid process and of electrorefining.

467. GRONNINGSÆTER, A. M. (assigned to Falconbridge Nickel Mines, Ltd.). Recovering Metal Values From Slags. U. S. Patent 2,438,911, Apr. 6, 1948; Chem. Abs., vol. 42, 1948, p. 6305i.

Converter slag obtained during the processing of high-grade Ni ores is admixed with slag and matte from the blast furnace and agitated with air and pulverized coal. The molten mass is allowed to pass into the quiet zone where the matte settles out and is separated. The slag is discharged into a second settler, where the final separation of matte and slag takes place. A similar procedure is followed in the reverberatory furnace process. In this instance the converter slag is returned and admixed with the reverberatory slag. These are conducted continually to a reducer-mixer, where the FeS, air, and fuel are added. Separation of the matte occurs as above. Co ores are similarly treated. Cu recovery is also accomplished but more severe treatment is required and a converter-type reducer-mixer is preferred. Examples from pilot-plant runs show Cu content of slag from the settler down to about 0.11 percent with Ni content down to as low as 0.07 percent.

468. GRONNINGSÆTER, ANTON, AND DRUMMOND, P. R. Notes on the Operation of the Basic Copper (and Copper-Nickel Converter). Trans. Canadian Inst. Min. Met., vol. 45, 1942, pp. 99-139 and 324-349 (in Canadian Min. and Met. Bull. Nos. 358 and 363); Chem. Abs., vol. 36, 1942, p. 6468⁵.

The factors affecting converter operation are discussed, including air efficiency, heat balances, converter fluxes, weight of converter slag, SiO₂ content of slag, cleaning of converter slag, influence of grade of matte, magnetite, and mechanical considerations. A careful study is reported covering a complete cast or cycle. All raw materials and products were weighed and analyzed. Material balances and thermal balances were calculated. Temperature control within rather narrow limits is the most important factor of good converter operation. Too high a temperature is hard on the lining. An excessively low temperature results in formation of magnetite and low O₂ efficiency. In spite of unavoidable high heat losses in the escaping gases, the converter is a fairly efficient thermal machine, and a substantial part of the total net heat available from the reactions can be expended on smelting cold fluxes.

469. GRÖNWALL, E. A. A. [Cobalt.] Swedish Patent 73,395, Jan. 12, 1932 (*see* Chem. Abs., vol. 26, 1932, p. 5059); Chem. Abs., vol. 27, 1933, p. 4208.

Sulfidic Cu ore is roasted and smelted, and the matte is bessemerized. The blowing in the converter is continued until Co or CoS has largely been oxidized and taken up by the slag. This slag is decomposed or leached with acid, for example, H_2SO_4 to extract the Co.

470. ———. [Extracting Cobalt From Sulfidic Copper Ore.] Swedish Patent 75,230, Sept. 6, 1932 (addition to Swedish Patent 73,395; Chem. Abs., vol. 27, 1933, p. 4208); Chem. Abs., vol. 27, 1933, p. 5297.

The residues containing Cu and precious metals obtained by the extraction of Co from the slag are mixed with the sulfidic ore and thus returned to the smelting process.

471. ———. [Extraction of Cobalt From Sulfidic Copper Ore.] Swedish Patent 76,502, Feb. 14, 1933 (addition to Swedish Patent 74,511; *see* Chem. Abs., vol. 27, 1933, p. 5297); Chem. Abs., vol. 28, 1934, p. 1975².

The slag is remelted with alkali or alkaline-earth sulfides, or with sulfides formed during the melting by the action of a carbonaceous reducing agent on added sulfites or sulfates. Free sulfur may be added to the slag.

472. ———. Cobalt and Cobalt Compounds From Copper Pyrites. British Patent 357,366, Sept. 17, 1929 (Chem. Abs., vol. 26, 1932, p. 3223); U. S. Patent 1,868,414, July 19, 1932; Chem. Abs., vol. 26, 1932, p. 5059.

The pyrites is roasted and melted to form a matte, the matte is bessemerized, and blowing is continued until most of the Co or cobalt sulfide has passed into the slag (which is then further treated to obtain Co or Co compounds). Numerous details and modifications of procedure are described.

473. I. G. FARBENINDUSTRIE, A. G. [Treating a Nickel Matte.] French Patent 850,651, Dec. 22, 1939 (*see* Chem. Abs., vol. 36, 1942, p. 1890³); British Patent 507,792, June 21, 1939; Chem. Abs., vol. 34, 1940, p. 361⁶.

A method of recovery of Ni from a Ni matte consists in subjecting the matte first to a thermal treatment at a temperature ranging from 400° to 900° C., preferably at about 700° C., and then to the action of appropriate solvents (acids, saline solutions).

474. INTERNATIONAL NICKEL CO. Bessemerizing Nickel Mattes. British Patent 349,700, Mar. 28, 1930 (*see* French Patent 694,092; Chem. Abs., vol. 25, 1931, p. 1791); Chem. Abs., vol. 26, 1932, p. 956.

475. ———. [Bessemerization of Mattes.] French Patent 694,092, Apr. 17, 1930; Chem. Abs., vol. 25, 1931, p. 1791.

Mattes of Ni or alloys containing Ni, such as Monel metal, are bessemerized to remove S and reduce the mattes by melting the matte in a converter and introducing a mixture of air and superheated steam. The matte is blown at 1,100° to 1,600° C.

476. INTERNATIONAL NICKEL CO., INC. [Nickel and Copper.] French Patent 696,456, May 8, 1930; Chem. Abs., vol. 25, 1931, p. 2678¹.

Cu and Ni are extracted from materials containing them, particularly mattes containing sulfides of Ni and Cu, by heating the materials in the presence of a flux to obtain a molten mass, which permits stratification to separate the material containing Ni from that containing Cu. The part containing Cu is heated in the presence of air to obtain porous Cu, and the part containing Ni is submitted to the carbonyl process to obtain Ni.

477. ———. [Recovering Copper and Nickel From Sulfide Mattes, etc.] German Patent 596,022, Apr. 26, 1934 (*Cl. 40a 43.01*) (*see* British Patent 351,150; Chem. Abs., vol. 26, 1932, p. 2688); Chem. Abs., vol. 28, 1934, p. 4363⁷.

478. JOHANNSEN, FRIEDRICH, AND SCHWARTZ, WERNER. [Separation of Iron From Arsenical Cobalt Speiss.] Bergakademie, Clausthal, Ger. *Erzbergbau u. Metallhüttenw.*, vol. 3, 1950, pp. 138-144; Chem. Abs., vol. 45, 1951, p. 2379a.

The separation of Fe from Co speisses proceeds according to the equation $\text{Fe} + \text{CoO} = \text{FeO} + \text{Co}$. The As content has almost no influence upon the equilibrium but prevents lowering of the working temperature and thus indirectly prevents improvement in the separation, since, with falling temperature, the equilibrium is displaced farther to the right. Experiments show that the S content of the ore interferes, while S obtained by the use of basic slags improves the Fe separation. Reverberatories are unsuited, but in converters the reaction proceeds quickly. By a suitable slag exchange, 98.88 percent of the Fe can be slagged, leaving about 80 percent of the Co in the speiss.

479. JOHNSON, G. W. (assigned to I. G. Farbenindustrie, A. G.) Working-Up of Nickel-Copper Mattes. British Patent 507,792, March 25, 1938; British Chem. Abs., 1939, p. B-955.

The preferential extraction of Ni from the matte with 20 percent HCl is improved by heating the matte (with exclusion of air) for 12 to 24 hr. at 700°-900° C. before leaching.

480. MINING JOURNAL (LONDON). Researches on Nickel Converter Practice. Vol. 239, July 4, 1952, pp. 13-14; Metals Rev., vol. 25, No. 9, September 1952, p. 15 (121-C).

Discusses different converter procedures, variations in handling nickel and cupronickel matte, and electrically heated converters.

481. MOND NICKEL CO., LTD., AND WALLIS, A. E. Nickel Carbonyl. British Patent 481,511, Mar. 9, 1938; Chem. Abs., vol. 32, 1938, p. 6812¹.

The matte from the "second bottoms" of the Orford process may be sintered by heat of oxidation of the sulfides and then reduced with a carbonaceous material, such as coal, coke, or heavy oil, to produce a feed material for direct formation of carbonyl with carbon monoxide under pressure.

482. SAVELSBERG, WALTER. [The Problem of Separating Copper and Nickel.] Metallbörse, vol. 22, 1932, pp. 257-258, 289-290, 353-354, 385-386, 417-418, 449-450, and 482; Chem. Abs., vol. 26, 1932, p. 3461.

Discusses ordinary processes for separating Ni and Cu, such as the Orford process, partial oxidation by regulated roasting to obtain soluble CuSO_4 and insoluble NiS, cementation by Fe or Ni, electrolysis, the Hybinette process, etc., from theoretical and practical viewpoints and reasons for their failure adduced. The J. Savelsberg process has been used successfully for 30 years. In it the Cu-Ni-bearing material is smelted to a matte; this is powdered, roasted, sintered, and resmelted to a more concentrated matte, which is then treated in a small converter. Leaching and subsequent treatments are covered.

483. SCHLECHT, HELMUT, AND SCHLECHT, LEO (assigned to I. G. Farbenindustrie, A. G.). Recovery of Copper and Nickel From Mattes. U. S. Patent 2,239,626, Apr. 22, 1941; Chem. Abs., vol. 35, 1941, p. 4721¹.

Describes process for beneficiating Ni-Cu mattes by chemically converting the Ni content and extracting it. The matte is first conditioned by a long-lasting heat treatment under substantially nonoxidizing and nonreducing conditions at 400°-900° C., where-

by the reactivity of the Ni with the extracting agent is considerably enhanced.

484. SHOFFSTALL, A. S., MUDGE, W. A., BAGSAR, A. B., AND BIEBER, C. G. (assigned to International Nickel Co.). Desulfurizing Nickel-Containing Matte. U. S. Patent 1,828,752, Oct. 27, 1932 (*see* Canadian Patent 311,539; Chem. Abs., vol. 25, 1931, p. 3304); Chem. Abs., vol. 26, 1932, p. 686.

485. SMIRNOV, V. I., AND CHELYSHEVA, N. L. [Roasting Nickel Matte in the Suspended State.] *Tsvetnye Metal*, No. 9, 1939, pp. 98-102; Chem. Abs., vol. 35, 1941, p. 61¹.

A study, on a laboratory scale, was made of roasting finely divided Ni matte in a suspended state, and on the basis of these results a semicommercial, two-stage unit was constructed. S could be reduced to 6.5 percent. Various factors affecting the operation are discussed, such as fineness of grind, temperature, furnace dimensions, etc.

486. STANLEY, R. C. (assigned to International Nickel Co.). Recovery of Copper and Nickel From Mattes, etc. British Patent 351,150, Aug. 17, 1929; Chem. Abs., vol. 26, 1932, p. 2688.

Sulfidic Cu- and Ni-bearing materials, such as mattes, are heated in the presence of a stratifying substance to effect melting and form the mass into Cu-bearing "tops" and Ni-bearing "bottoms." Pure Cu and Ni are recovered in a dry way from these materials. The smelting may be effected with sodium sulfide or a mixture of salt cake and coke, or calcium sulfide. In a modified multistage process, the copper sulfide "tops" of the second stage may be returned to the first melting stage and the Ni-"bottoms" of the first stage smelted with addition of fresh flux in the second stage. Various details of the procedure are described, including the recovery of Ni as carbonyl, decomposition of the latter, and reuse of the CO involved.

487. — (assigned to International Nickel Co., Inc.). Recovery of Nickel. Canadian Patent 315,060, Sept. 8, 1931; Chem. Abs., vol. 26, 1932, p. 1566.

A material containing nickel and copper sulfides is mixed with Na₂S and subjected to heat to form a fused mass in which the bulk of the CuS stratifies from the bulk of the NiS, the NiS being contaminated with CuS. The NiS is separated from the CuS and oxidized, and the oxidized material is reduced to impure metallic Ni containing metallic Cu without utilizing wet processes. CO is passed in contact with the impure Ni at 80°-100° C. to volatilize the Ni as carbonyl, which is decomposed at 125° C. to approximately 250° C. to recover virtually pure metallic Ni free from Cu.

488. — (assigned to International Nickel Co.). Nickel From Ores or Mattes. U. S. Patent 1,854,234, Apr. 19, 1932 (*see* Chem. Abs., vol. 26, 1932, pp. 1566 and 2688); Chem. Abs., vol. 26, 1932, p. 3223.

Nickel sulfide from Ni-Cu ores or mattes is concentrated by smelting with an alkali sulfide to effect separation of nickel sulfide from copper sulfide. The concentrated nickel sulfide is roasted to oxidize Ni; nickel oxide is reduced to Ni by a gaseous reducing agent; the Ni is volatilized as nickel carbonyl; and the nickel carbonyl is decomposed to produce commercially pure Ni.

489. TAFEL, V., AND LOOSE, H. W. [Reactions in the Removal of Arsenic From Speiss by Heating in the Presence of Pyrites.] *Metall u. Erz*, vol. 28, 1931, pp. 422-425; Chem. Abs., vol. 25, 1931, p. 5882⁹.

By heating a mixture of arsenides and pyrites in the presence of air, As can be completely removed. With a 1:1 mixture, the temperatures required were 700°-800° C. for Cu₃As, 900° C. for FeAs, and 1,100° C. for NiAs. FeS can be used in place of pyrites. The re-

moval of As is attributed partly to the reducing action of SO₂ and partly to decomposition of arsenates and arsenites by SO₂. In atmospheres such as CO, CO₂, and N₂, the As can also be removed by heating with pyrites, such volatile compounds being formed as As₂S₃ and As₂S₅.

490. TSEIDLER, A. A., AND DAMSKAYA, G. I. [The Causes of Caking of Nickel Matte in Roasting.] *Tsvetnye Metal*, vol. 15, 1940, pp. 75-78; Chem. Zentralb., vol. I, 1942, p. 1934; Chem. Abs., vol. 37, 1943, p. 4664⁹.

In laboratory experiments, samples of Ni matte (150-200 gm.) containing 75.04 percent Ni and 22.72 percent S placed in the muffle furnace in a N₂ atmosphere did not increase in weight or cake; this indicates that, in ordinary roasting, oxidation of the included metallic Ni occurs. The nickel sulfide oxidizes slowly but undergoes recrystallization with formation of a eutectic of two nickel sulfides. These changes in structure cause caking of the matte at low roasting temperatures (400°-500° C.). The addition of previously roasted matte as a remedy is ineffective. A more effective remedy is a slow increase of the temperature and thorough mixing.

491. URAZOV, G. G., MOROZOV, I. S., AND USTAVSHCHIKOVA, G. U. [Experimental Investigation of Chloridization of Copper-Nickel and Iron-Bearing Matte.] *Tsvetnye Metal*, vol. 10, No. 6, 1935, pp. 109-130; Chem. Abs., vol. 30, 1936, p. 8109³.

In smelting, Fe and S are lost, while in the chloridization scheme both can be recovered; the authors studied chloridization chemistry, separation of resulting chlorides, and a general scheme for inclusion in a metallurgical Ni-Cu process for use on Ufalie mattes. Chlorination may be accomplished using either anhydrous chlorine gas or sulfur chloride (which is produced in the process). Volatilization temperatures, conditions for various chlorides, and reports on electrolysis of the chlorides are included.

492. ZAKHAROV, V. [Desulfurization of Nickel Matte in the Induction Furnace.] *Tsvetnye Metal*, No. 12, 1932, pp. 50-52; Chem. Abs., vol. 27, 1933, p. 5693.

Desulfurization of Ni matte can be accomplished by blowing the matte in an induction furnace, or simply by passing an air stream over the surface of the melt. The S was lowered to 0.5-0.3 percent. It is believed that desulfurization can be carried further if a suitable crucible-lining material is found. Zakharov used crucibles lined with zirconia or magnesite, or graphite crucibles lined with magnesite or magnesite and tar. None of these, however, lasted more than 2 to 3 hr. at the melting temperatures.

ROASTING WITH A SALT OR SALT-FORMING GAS

493. BORCHIERS, HEINZ. [Working Up Low-Grade Nickel Ores.] *Metall u. Erz*, vol. 33, 1936, pp. 435-441; Chem. Abs., vol. 30, 1936, p. 8109⁹.

Using sulfidic low-grade Ni ores, a study was made of sulfatizing, roasting, and chlorination. Chlorination with either salt or chlorine gas was unsuccessful. By employing hydrochloric or sulfuric acids, Ni was leached out at room temperatures, but Cu was substantially insoluble. At a higher temperature (400° C.) Ni dissolved, while copper and iron chlorides volatilized, effecting a separation.

494. BROWN, R. G. (assigned to The Sulphide Corp.). Separation of Metals by Selective Oxidation of the Chlorides. Canadian Patent 318,896, Jan. 12, 1932; Chem. Abs., vol. 26, 1932, p. 1890.

Nickel and cobalt are separated by treating a mixture of the anhydrous chlorides with an oxidizing gas

in the presence of enough Cl_2 to inhibit oxidation of the NiCl_2 while permitting oxidation of CoCl_2 . The NiCl_2 is separated from the Co oxide; the chloride is oxidized in the presence of excess air; the liberated Cl_2 and air mixture is recycled into contact with fresh chlorides.

495. BROWN, R. G. (assigned to Sulfur & Smelting Corp.). Separating Metals Such as Nickel and Copper by Selective Oxidation of Their Chlorides. U. S. Patent 1,933,702, Nov. 7, 1934; Chem. Abs., vol. 28, 1934, p. 454⁷.

A mixture of oxidizable anhydrous metal chlorides, including chlorides of Ni and Cu or Co, is treated with an oxidizing gas such as air at a temperature promoting oxidation, and enough Cl_2 is introduced into the reaction zone to inhibit oxidation of at least one of the chlorides of lesser reactivity with O_2 , while oxidizing other chlorides present.

496. DUFFIELD, F. L. Nickel, Copper, Iron, etc., From Sulfide Ores. British Patent 328,696, Feb. 8, 1929; Chem. Abs., vol. 24, 1930, p. 5279⁷.

Sulfide ores containing Ni are heated, after crushing, to 700°–1,000° C. with an excess of air to burn the undesired S and convert the Fe to oxide or sulfate; an easily decomposable chloride, such as MgCl_2 , is then added, and the oxidizing roast is continued at a temperature not exceeding 650° C. to form chlorides of metals such as Ni, Cu, Ag, and Pd that may be volatilized and condensed in water. The remaining charge is reduced, Fe is separated magnetically, and the residue is treated for recovery of Au and Pt. The chloride solution may be electrolyzed or otherwise treated. (Various details of the treatments for recovery of different metals are given.)

497. FINCKE, H. [Sodium Sulfide Fusions.] Metallbörse, vol. 17, 1927, pp. 2637–2638; Chem. Zentralbl., vol. I, 1928, p. 481; Chem. Abs., vol. 23, 1929, p. 4914⁴.

The behavior of PbS , ZnS , Cu_2S , FeS , and Ni_3S_2 when fused with Na_2S was investigated. PbS dissolved, but ZnS did not. A mixture of $\text{ZnS} + \text{PbS}$ remained at the bottom of the fused Na_2S without completely dissolving. Metallic Cu or Pb was not obtained by fusion of the sulfides with Na_2S . Somewhat better results were obtained by fusion of Cu_2S and PbS with Na_2SO_4 and charcoal. Similar to the Orford process, fusion with $\text{Na}_2\text{SO}_4 + \text{C}$ gave better separation of nickel and copper sulfides and than when fused with Na_2S alone. The complete separation of Cu_2S from PbS in a Pb matte cannot be accomplished by a Na_2S fusion because of the FeS , which is also present.

498. FINCK, C. G., AND VIVIAN, R. E. Treatment of Nickeliferous Sulfides. Canadian Patent 321,511, Apr. 19, 1932; Chem. Abs., vol. 26, 1932, p. 3223.

Ground nickeliferous sulfide material containing Fe, Cu, and precious metals is heated to 320° C., and dry Cl_2 is passed over the mass for 20 minutes per quarter-inch thickness of material to convert the Fe, Ni, and Cu into chlorides. The temperature is controlled at 320° C. to volatilize the iron chloride. The vapors of iron chloride are heated with air at 300° C. to form oxides of Fe, and the Cl_2 is recovered for reuse. The ground residual mass is leached to remove soluble compounds of Ni, Cu, Pt, and Pd. The leached solution is treated by cementation to precipitate Pt and Pd and then electrolytically to precipitate Cu. The Ni is recovered by electrolytic precipitation. Precious metals are recovered from the insoluble residue.

499. GRAHAM, M. E., AND BEIDLER, E. A. (assigned to Republic Steel Corp.). Ferrous Chloride. U. S. Patents 2,677,593, 2,677,594, 2,677,595, 2,677,596, 2,677,597, 2,677,606, and 2,677,607, May 4, 1954; Chem. Abs., vol. 48, 1954, p. 14138f.

Patent 2,677,593. In preparing substantially pure FeCl_2 , the FeCl_2 is separated from mixtures with NiCl_2 (in which the major component is FeCl_2) by introducing the mixture in nongaseous form into a reaction zone, providing sufficient metallic Fe to combine with all the Cl in the NiCl_2 to produce Ni and additional FeCl_2 , and elevating the temperature slowly so that substantially all of the FeCl_2 is vaporized.

As indicated in *Patent 2,677,594*, the mixture in gaseous form is passed through gas-pervious solid or molten Fe to reduce the NiCl_2 to nonvolatile Ni, while the substantially pure FeCl_2 remains in gaseous state.

Patent 2,677,595 relates separation of FeCl_2 from CoCl_2 by a similar transfer action, in which the metallic Fe (in an amount at least three times that required theoretically to combine with all the Cl in the CoCl_2) is added to a nongaseous mixture of FeCl_2 and CoCl_2 to produce metallic Co and additional FeCl_2 . All of the FeCl_2 can be vaporized in a substantially pure state.

Patent 2,677,596 indicates that FeCl_2 is removed from CoCl_2 by passing the mixture in gaseous form through a gas-pervious solid or liquid Fe to reduce the CoCl_2 to nonvolatile Co, while the substantially pure FeCl_2 remains in gaseous form.

Patent 2,677,597 indicates that FeCl_2 is separated from mixtures with metallic Co, without appreciable loss of Co in the form of CoCl_2 , by introducing the mixture of FeCl_2 and Co into a sublimation zone wherein at least the same weight of metallic Fe is present as Co in the original mixture, increasing the temperature to vaporize all the FeCl_2 and separating the volatilized FeCl_2 by passing it from the zone to leave only metallic Fe and Co in the sublimation zone.

In *Patent 2,677,606*, FeCl_2 is separated from mixtures with metallic Ni in exactly the same manner as it is separated from mixtures with metallic Co in *Patent 2,677,597*.

In *Patent 2,677,607*, NiCl_2 is selectively reduced from a mixture of commercial NiCl_2 and FeCl_2 to produce pure Ni. The mixture of NiCl_2 and FeCl_2 is introduced into a reducing zone in finely divided form and heated between 450° and 650° C. A reducing gas consisting of H_2 and HCl is introduced into the reducing zone. The H_2 reduces the NiCl_2 to Ni while the HCl has a strong retarding effect upon the competing reaction wherein FeCl_2 would otherwise be reduced to Fe.

500. HARDIEK, WM. (assigned to Davison Chemical Corp.). Copper and Cobalt Recovery From Ore Composed Largely of Iron Sulfide. U. S. Patent 2,090,388, Aug. 17, 1937; Chem. Abs., vol. 31, 1937, p. 7025⁷.

Describes apparatus for use in a method of recovering Cu and Co from ore comprised primarily of FeS . While S is being roasted out of the ore, iron sulfate is introduced to convert Co and Cu to soluble forms, with little or no outside application of heat. However, the iron sulfate must not be added before the S has burned off somewhat to avoid reduction of the sulfate. The soluble Co and Cu values are then recovered from the completely roasted ore.

501. HOHN, HANS, HORAK, OTTO, AND SCHMIEDL, ERNST (assigned to Kupferbergbau Mitterberg, G. m. b. H.). [Working Up Sulfide Ores by Chlorination.] Austrian Patent 179,095, July 10, 1954; Chem. Abs., vol. 48, 1954, p. 9303e.

Sulfidic iron ores (for example, pyrite) are treated by chlorination. Thus, 1,000 kg. of completely dried powdered pyrite concentrate was chlorinated in 2 portions and in countercurrent flow in reaction towers with 781.4 kg. of 90–100 percent Cl_2 (3 percent excess) at a reaction temperature of 350° C. to obtain 1,104.7 kg. of FeCl_3 (I) and 486.7 kg. of S_2Cl_2 (II), an amount sufficient to chlorinate the second portion to give S , FeCl_3 (III), and CuCl_2 (IV), and NiCl_2 (V), and gangue 52.3 kg. was obtained, and the nonvolatile por-

tion was returned to the first step, where (III) was converted into volatile (I), a separation of Fe, S, and Cu plus Ni being so performed. The whole of (I) was then burned at 850° C. to give 556.5 kg. of ferric oxide pigment and 724.6 kg. of Cl₂ (92.7 percent of the starting amount). The remaining Cl₂ was regenerated by electrolysis of the aqueous solutions of the IV and V and returned to the process. An Ni-containing pyrite, Ni 7.5, Cu 0.4, S 25.5, Fe 42.6, siliceous gangue 23 percent, and Pt 120 gm. per ton was treated by the same process.

502. MACKLIN, P. E. (assigned to Rideau Smelting & Refining Co., Ltd.). Treatment of Cobalt Ores. Canadian Patent 298,531, Mar. 18, 1930; Chem. Abs., vol. 24, 1930, p. 2709³.

Co and Ag are recovered from Co ores by crushing and concentrating the ores, heating with 5 percent of an alkali metal salt, to about 1,100°–1,200° F., then heating the mass with a gas containing H₂ for about 4 to 6 hr. to drive off the As and S, melting the mass and pouring it into molds, removing the slag, and separating the Ag from the bottom of the mold and separating and recovering the Co and other metals from the upper layers of the mold.

503. MILLER, E. B., AND CONNOLLY, G. C. (assigned to Davison Chemical Co.). Separating Cobalt From Ores. U. S. Patent 1,922,490, Aug. 15, 1933; Chem. Abs., vol. 27, 1933, p. 5046.

An ore containing Co, together with ores of other metals, such as Fe pyrites ore, is roasted at a temperature below that at which the sulfate of Co decomposes, but above that at which the sulfate of Fe decomposes, and while, at such a temperature, SO₂ is introduced to react with the mass and form cobalt sulfate which is subsequently leached out of the product.

504. SCHAAL, R. B. (assigned to Ferro Enamel Corp.). Refining of Cobalt Ores. U. S. Patent 2,379,659, July 3, 1945; Chem. Abs., vol. 39, 1945, p. 4043⁶.

The Co ore is refined by mixing it with NaCl, soda, and KNO₃ and fusing at 1,200°–1,300° F. It is necessary to remove As and S completely from Co ore as their presence renders the Co objectionable for use in the ceramic industry or for enamel frits. The NaCl enables the ore to be fused during the treatment. Soluble salts of As and S (sodium arsenate and sodium sulfate) are formed, which may be removed by leaching with H₂O while the metal content of the ore is converted to insoluble oxides. The As and S are then treated with hot milk of lime to recover the As, as well as NaOH, as byproducts. The metal oxides are dissolved in HCl to recover the Co and other metals. CaCO₃ is added to precipitate Fe, Pb, SiO₂, and any residual arsenic, while the Co, Ni, and Cu are left in solution as chlorides. The NaOH from the arsenic treatment is mixed with the Co solution to a pH of 8.3–8.8 to precipitate the Co, Ni, and some of the Cu and Mn as basic carbonates. They are dried at 500°–1,000° F. to give a product with Co 40–50, Ni 10–20, Cu 1–3, and Mn 0.5–2.5 percent. These metals may be separated further by known processes.

505. TAFEL, VICTOR. [Nickel Recovery.] German Patent 693,519, June 13, 1940 (*Cl. 40a 2.60*); Chem. Abs., vol. 35, 1941, p. 4721².

The Ni ore with added NaCl is roasted at 375° C. in the presence of SO₂. The SO₂ is prepared separately from the roaster gases.

506. TAFEL, VICTOR, AND LAMPE, G. [The Conversion of the Nickel Content of Various German Nickel Ores and Minerals Into Soluble Form.] *Metallwirtschaft*, vol. 16, 1937, pp. 1038–1041; Chem. Abs. vol. 32, 1938, p. 89⁸.

Roasting ores and minerals from the Frankenstein district in oxygen-enriched air containing SO₂ or SO₃

make a large part of the Ni water-soluble. Addition of NaCl to the ore helps in some instances.

507. WILENCHIK, I. W. Separating Copper From Nickel. U. S. Patent 1,703,329, Feb. 26, 1929; Chem. Abs., vol. 23, 1929, p. 1864⁹.

An alloy containing Cu and Ni is melted, with a mixture of S, Na₂SO₄, CaSO₄, and coke; the molten mass is poured into a settler, so that on cooling the sulfides of Cu and Ni separate by gravity and may be separated and converted successively into oxides and metals.

508. ZIELINSKI, EMIL. [Investigation of the Conditions for the Chloridizing Volatilization of Metals.] *Arch. Erzbergbau Erzaufbereit. Metallhüttenw.*, vol. 1, 1931, pp. 31–41; Chem. Abs., vol. 28, 1934, p. 437⁶.

Samples were exposed in a glass or porcelain boat to a stream of specially purified Cl₂ and heated in an electric muffle. Chloridizing starts, for FeS, Cu₂S, and CoS, below room temperature and for Ni₂S₃ at 150° C. Chloridation is complete for FeS at 250° C., CoS at 700° C., and Ni₂S₃ at 550° C. Both CuCl and CuCl₂ are formed. Cuprous chloride reaches a maximum of 22 percent of the total chlorides at 400° C. At 570° C. the sample is 100 percent CuCl. At 880° C. CuCl₂ has reverted to CuCl. The physical condition of the sample is important. In the presence of small amounts of water and C, chloridization is accelerated. The process is more complete at a given temperature when more of the surface of the sample is exposed. NaCl begins reacting with metals and oxides at 500° C., with sulfides at 350° C. The presence of S makes the oxides much easier to chloridize with NaCl.

SMELTING TO FERROALLOYS

509. AVERY, J. M. (assigned to Arthur D. Little, Inc.). Smelting Complex Copper-Nickel-Iron Sulfide Ores. U. S. Patent 2,261,946, Nov. 11, 1942; Chem. Abs., vol. 36, 1942, p. 975⁸.

A matte is formed containing most of the metal values of the ore. The matte is roasted; the resulting mixed metal oxides are smelted by selective reduction in an electric furnace of the submerged arc-resistance type to produce metallic Cu and a Ni-rich slag. This slag is smelted to produce ferronickel.

510. GRÖNWALL, E. A. A. [Extracting Cobalt From Sulfidic Copper Ores.] Swedish Patent 74,688, July 5, 1932 (*see* Chem. Abs., vol. 27, 1933, p. 4208, and the following abs.); Chem. Abs., vol. 27, 1933, p. 5297.

The ore is roasted and smelted, and the matte is bessemerized, blowing being continued until a major part of Co or CoS present is oxidized and taken up by the slag. The slag thus obtained is smelted with carbonaceous material by which an alloy containing Co is produced.

PYRO SLAGS

GENERAL

511. DAMSKAYA, G. I. [Viscosity of Slags on Non-ferrous Metallurgy.] *Akad. Nauk, S. S. S. R. Otdel. Tekh. Nauk, Inst. Mashinovedeniya, Soveshchaniye, Vyazkosti, Zhidkosti i Kolloid, Rastvorov* (Conf. on Viscosity of Liquids and Colloidal Solutions), vol. I, 1941, pp. 295–305; Chem. Abs., vol. 40, 1946, p. 5372⁶.

Slags from Ni-producing plants are considerably more viscous than Cu-production slags. The addition of SiO₂ or MgO tends to raise the viscosity; with MgO, especially, the temperature coefficient is high. The effect of adding FeO is to lower the viscosity. The assays of slags with the corresponding viscosities are discussed.

- 512.** DAMSKAYA, G. I., AND TSEIDLER, A. A. [Viscosity of High-Magnesium Slags From Smelting Nickel.] *Tsvetnye Metal*, vol. 19, No. 3, 1946, pp. 31-33; *Chem. Abs.*, vol. 41, 1947, p. 1968a.

The MgO content of the slags was 7.8-17.9 percent. The temperature range at which the viscosity was measured was 1,350°-1,250° C. The viscosity increased with the MgO content. The increase was smaller at the higher temperatures and sharp as the temperature decreased. As the MgO content rose above 15 percent, the viscosity rose sharply. The viscosity of the high-MgO slags could not be determined below 1,290° C. because they solidified. The SiO₂ varied from 38.14 to 44.75 percent. The temperature-effect curves of slags with varying SiO₂ were almost parallel and generally not as steep as similar curves for MgO. Increasing the FeO from 15.4 to 20.4 percent lowered the viscosity by 30 percent at 1,300° C. and by 44 percent at 1,250° C. The results are tabulated and presented on curves.

- 513.** DREV, N. P., KOCHNEV, M. I., KOCHIN, M. F., AND GYRDYMOV, YU. A. [Effect of Alkali Metal Oxides on the Viscosity of High-Magnesia Slags.] *Isvest. Akad. Nauk. S. S. S. R. Otdel. Tekh. Nauk*, 1952, pp. 1182-1188; *Chem. Abs.*, vol. 47, 1953, p. 8009i.

The viscosity of slags produced during melting of Ni ores in a shaft furnace was determined at 1,203°-1,480° C. The slags contained SiO₂ 41.13-48.00, Al₂O₃ 7.97-11.55, CaO 14.86-18.13, FeO 9.86-16.35, MgO 13.58-19.61, and Na₂O (added as Na₂SO₄) 0-2.32 percent. Low-FeO (10-12 percent) and high-MgO (17-19 percent) slags were too viscous for satisfactory furnace operation; the viscosity of these slags was greatly reduced by the addition of 1.5-2.0 percent Na₂O provided the SiO₂+Al₂O₃ content did not exceed 52 percent. Slags containing Na₂O had a lower Ni content than similar slags without Na₂O.

- 514.** DOWNIE, C. C. Nickel Slags. *Min. Mag.*, vol. 85, October 1951, pp. 212-214; *Metals Rev.*, vol. 25, No. 1, January 1952, p. 20 (5B).

Properties, treatment, and utilization are discussed.

- 515.** GUERREIRO, ARYKERNER. [Slags in the Metallurgy of Nickel.] *Rev. chim. ind.* (Rio de Janeiro), vol. 8, No. 87, pp. 17-19 and 313-315; *Chem. Abs.*, vol. 33, 1939, p. 8538⁶.

Methods of calculating furnace charges are outlined.

- 516.** GUSTAFSSON, E. G. T. Melting Iron-Group Metals and Alloys in Electric Furnaces. U. S. Patent 1,902,638, Mar. 21, 1933. *Chem. Abs.*, vol. 27, 1933, p. 3148.

In an electric furnace with a movable vertical electrode, the slag is allowed to cover the charge of oxide ore and reducing agent. The heat required is developed by the electrical resistance of the slag and is also augmented by an arc.

- 517.** KALLING, BO M. S., AND BRANNSTROM, PER G. L. Treatment of Metallurgical Slags. U. S. Patent 2,295,219, Sept. 8, 1943; *Chem. Abs.*, vol. 37, 1943, p. 1119².

A process is employed for recovering the Au, Ag, Cu, Ni, and Co from siliceous slags, which involves adding metallic Fe and iron sulfide and mixing at a temperature (suitably about 1,200°-1,300° C.) at which these materials are in a molten state. The iron sulfide used should have a composition corresponding to a higher content of nonoxidizing Fe than that of the formula FeS.

- 518.** LATHE, F. E. The Role of Alumina in Slags. *Trans. Canadian Inst. Min. Met. Eng.*, vol. 54, 1951, pp. 165-173 (in *Canadian Min. Met. Bull.* 467); *Chem. Abs.*, vol. 45, 1951, p. 7933i.

A discussion based largely on the FeO-SiO₂,

FeO-Al₂O₃-SiO₂, CaO-Al₂O₃-SiO₂, equilibrium diagrams is presented. The composition of blast-furnace slags, Cu and Cu-Ni blast-furnace slags, and basic open-hearth slags are discussed (36 refs.).

- 519.** OELSON, WILLY. [Experimental Studies on Metal-Slag Reactions.] *Erzbergbau u. Metallhüttenw.*, vol. 2, 1949, pp. 328-334 (see *Chem. Abs.*, vol. 44, 1950, p. 1375f); *Chem. Abs.*, vol. 44, 1950, p. 1864h.

A review of the results of investigations conducted chiefly by Oelson and others during the past 15 years, deals chiefly with the metallurgy of Cu, Co, Ni, Al, Cr, V, Cb, and Ta. Equilibrium in metal-slag reactions are discussed, as well as the effect of temperature on the equilibrium reciprocal solubility of metal melts and their slags, action of Mn and Si as deoxidizers for steel melts, equilibrium between Cu melts and copper-iron silicates, equilibrium between Cu melts and copper phosphates, deoxidation of Cu with P, influence of base metal upon the metal-slag reaction, heats of formation of alloys and their melts, separation in slags, equilibrium between fused metals and sulfide slags, behavior of Al in raw Fe baths toward sulfide slags (14 refs.).

- 520.** STAHL, W. [Nickel Slagging in Copper Refining With the Formation of Ferrites.] *Metall u. Erz.*, vol. 28, 1931, pp. 55-56; *Chem. Abs.*, vol. 25, 1931, p. 2084.

In the presence of Fe it is comparatively easy to remove Ni from Cu by slagging it out as ferrites (Ni Fe₂O₄ and Ni FeO₃). The residual Cu retains a Ni content of 0.10-0.15 percent, which cannot be removed in this manner.

- 521.** VOGEL, RUDOLF, AND ROSENTHAL, K. [The System Iron-Cobalt-Cobalt Silicide-Iron Silicide.] *Arch. Eisenhüttenw.*, vol. 9, 1935, pp. 293-299; *Chem. Abs.*, vol. 30, 1936, p. 1011².

The ternary system Fe-Co-Si was studied thermally and microscopically in the range Fe-Co-CoSi-FeSi. The compounds FeSi and CoSi form an uninterrupted series of solid solutions. The existence of a ternary compound, FeCoSi, was established; two subregions are distinguished—Fe-Co-Co₂Si-FeCoSi-FeSi and FeSi-FeCoSi-Co₂Si-CoSi. Describes crystallization.

FROM OXIDIZED ORES

- 522.** HILGERS, WILLY (Technische Hochschule, Aachen, Germany). [Metallurgical Study of the Reduction of Cobalt Mixed Oxide and the Refinement of Raw Cobalt.] *Erzbergbau u. Metallhüttenw.*, vol. 3, 1950, pp. 334-351; *Chem. Abs.*, vol. 45, 1951, p. 1478i.

In the reduction of mixed cobalt oxides, low carbon produces a brown slag, rich in Fe and Mn and poor in Co. Addition of CaO and quartz is necessary to obtain a slag of high fluidity. Such a slag is favorable to the removal of Mn. Removal of S is favored by lower temperatures and addition of dissolved CaO and quartz. Fe removal is carried out at higher temperatures with a slag high in CaO and quartz (16 refs.).

- 523.** LANGE, W., AND KOHLMAYER, E. J. [Nickel Oxide in the Metallurgy of Nickel.] *Metallwirtschaft*, vol. 16, 1937, pp. 598-602; *Chem. Abs.*, vol. 32, 1938, p. 937.

Atmospheric O₂ has been found to convert Ni to NiO both in converter blasting and in Cu refining of Ni and Sn alloys. This oxide dissolves in metallic melts, and after saturation separates as a complex slag of NiO and Cu₂O. The points of congelation of this slag are very close to those of NiO.

- 524.** TSEIDLER, A. A. [The Composition of Slag in the Ufaei Nickel Plant.] *Tsvetnye Metal*, No. 9, 1936, pp. 61-66; *Chem. Abs.*, vol. 31, 1937, p. 2141⁶.

FROM NONOXIDIZED ORES

525. ASENTI, PAAVO. [Thermal Properties of Cobalt Compounds and Their Appearance in Slags.] *Valtion Tek. Tutkimuslaitos, Julkaisu*, vol. 8, 1948, 84 pp. (in German) (see *Chem. Abs.*, vol. 46, 1952, p. 7865e); *Chem. Abs.*, vol. 46, 1952, pp. 7951f-7952e.

Various systems were studied with the object of recovering small amounts of Co from slags produced in smelting sulfidic Cu and Fe ores. The systems containing sulfides and oxides of Co, Fe, Cu, and Ni were studied at various temperatures and the solubilities reported. In general, Co will rob iron sulfide of its S, and Cu in turn has a still greater affinity for S. The presence of large quantities of Fe is detrimental because the sulfides of Co, Ni, and Cu are very soluble in it. An experiment, introducing iron pyrites to recover Cu, Co, and Ni was not quantitatively successful. However, some Ni, Cu, and Co were found in the matte. An industrial procedure for the treatment of oven slags is outlined.

526. DAVIS, W. C. Slag Losses in the Sudbury District. *Canadian Min. Jour.*, vol. 51, 1930, pp. 662-664; *Chem. Abs.*, vol. 24, 1930, p. 4490¹.

Slag losses vary inversely as the degree of silicate. Polybasic slags are more fusible than slags with a single base. Conditions at Sudbury are summarized; slag losses continue to constitute one of the principal sources of loss of metal in the Sudbury field.

527. DIEV, N. P. [Recovery of Cobalt From Converter Slags.] *Russian Patent* 65,071, Aug. 31, 1945; *Chem. Abs.*, vol. 40, 1946, p. 7145¹.

To obtain a matte containing most of the Co in the slag a sufficiently long contact of the components in the melt, mechanical action to cause coagulation of the fine particles, and thorough degasification of the melt are necessary. Good results are obtained by adding a small quantity of flux to the molten converter slag and passing through it a mixture of oil and finely divided S.

528. DOWNIE, C. C. Nickel Slags. *Min. Mag.*, vol. 85, 1951, pp. 212-214; *Chem. Abs.*, vol. 46, 1952, p. 72a.

Products made by utilizing slags from Ni smelting generally have greater strength and toughness than is common to the general run of slags. Nickel ores are usually rich in magnesium and chromium oxides, and in the ordinary way the high melting characteristics of these require excessive fluxing material. Electric smelting is not always economical. With a certain type of Greek ore, containing up to 15 percent Cr and 3-5 percent Ni, the Cr is eliminated by wet extraction. Standard dichromate practice is used, but the difference consists in the use of low-grade ores instead of the normal ones with some 40 percent of chrome oxides; as a result of treatment, the Ni contents in the residues are increased and the infusible contents eliminated. After the residues are briquetted, they are smelted in water-jacketed blast furnaces to give a 30-40 percent Ni matte, with comparatively easily fusible slags throughout. Some of the good and bad points about electric smelting are discussed.

529. GOLDMAN, K. M., DERGE, G., AND PHILBROOK, W. O. Effect of Silicon, Manganese, Phosphorus, Aluminum, Carbon, Nickel, and Copper on the Mechanism of Sulfur Transfer Across a Slag-Metal Interface. *Jour. Metals*, vol. 6, May 1954; *Trans. AIME*, vol. 200, May 1954, pp. 534-540; *Metals Rev.*, vol. 27, No. 7, July 1954, p. 28 (167-B).

The kinetics and mechanism of S transfer at a slag-metal interface are studied under laboratory control. Graphs, tables, diagrams, and micrographs are included (16 refs.).

530. KIRSEBOM, G. N. [Arsenic and Arsenic Compounds in Metallurgy.] *Tids Kjeml. Bergvesen*, vol. 20, 1940, pp. 1-7 (see *Chem. Abs.*, vol. 33, 1939, p. 4560¹); *Chem. Abs.*, vol. 35, 1941, p. 7331⁵.

A discussion and experimental study of the reduction of the metals Ag, Hg, Bi, Cu, Sb, Pb, Ni, Co, and Cd from their oxides or sulfides by As or As₂O₃ in the presence of molten NaOH is given. A 100-percent excess of caustic soda was necessary in order to secure a fluid slag over the metal with oxides and a larger excess with sulfides. Data are presented to show that the metal yield was high. However, because of the high caustic soda requirement, most of these reactions have found no practical application except in the case of the complex speisses and in the Cd industry in the treatment of flue dusts containing As, or As₂O₃, and CdO. They are also applied in preparing Ni-Cd alloys.

531. LICHTY, L. J. (assigned to Northfield Mines, Inc.). Recovery of Metals From Sulfur-Containing Metallurgical Slags. *British Patent* 682,832, Nov. 19, 1952; *Chem. Abs.*, vol. 47, 1953, p. 6852h.

Slag produced by blowing Cu matte in a converter contains 45-55 percent FeO, 18-30 percent SiO₂, and 2-5 percent Cu. The latter can be recovered as a sulfide by adding to the molten slag Si or an Al-Si alloy in the amount equal to about 20 percent of the element necessary for complete reduction of all FeO, and separating the resulting matte by settling. When nickel-bearing slag is used, Ni may be recovered in the same way.

532. OEISEN, W., AND KREMER, G. [Behavior of Melts of Iron, Nickel, and Manganese Toward Their Liquid Silicates and Solid Silicic Acid at 1,600° C.] *Mitt. Kaiser-Wilhelm-Inst. Eisenforsch.*, vol. 18, 1936, pp. 89-107; *British Chem. Abs.*, 1937, p. A-413.

Equilibria in the 3-phase system metal layer-silicate slag-solid SiO₂ have been determined for the components Fe-Ni-Mn-Si-O at 1,600°-1,650° C.

533. SMIRNOV, V. I., AND MISHIN, V. D. [Investigation of the Converter Slag in Nickel Recovery.] *Tsvetnye Metal*, vol. 16, No. 5, 1941, pp. 24-27; *Chem. Zentralb.*, vol. II, 1942, p. 2410; *Chem. Abs.*, vol. 38, 1944, p. 1987².

Slags produced in the converter smelting of mattes or other metallurgical products are discussed as initial slags and final slags. The loss of Ni or Co to these slags can be minimized by suitable metallurgical practices; they may be partly recovered by slag segregation followed by flotation.

534. YOSHII, YATARO, AND NAKABE, SANAI (assigned to Ikwa Mining Industries Co.). [Melt Rich in Cobalt.] *Japanese Patent* 178,191, Mar. 18, 1949; *Chem. Abs.*, vol. 45, 1951, p. 6149g.

535. ZUR STRASSEN, H. [Effect of Sulfur Upon the Equilibrium in Fusion of Fe+NiSiO₃=Ni+FeSiO₃.] *Ztschr. anorg. allgem. Chem.*, vol. 200, 1931, pp. 46-56 (see *Chem. Abs.*, vol. 24, 1930, p. 5581); *Chem. Abs.*, vol. 26, 1932, p. 21.

The equilibrium $\text{Fe} + \text{NiSiO}_3 \rightleftharpoons \text{Ni} + \text{FeSiO}_3$ is displaced slightly in the presence of S in that the potential difference between Fe and Ni becomes smaller. Since the equilibrium follows the ideal mass-action law, addition of S has only the effect of a metallic diluting agent. If the S concentration becomes greater than 0.5 mole per mole of metal, it has a strong reducing action upon the metallic oxide in the silicate phase. Slags with a high concentration of NiO are strongly reduced.

Metallic sulfide melts exhibit a high solvent action for NiO, much less for FeO. This unequal solubility of the oxides leads to secondary reactions, which, in melts with the Ni-rich slags, produce deviations from

the ideal mass-action law. The presence of oxide in the regulus shows that the NiSiO_3 in the melt is largely dissociated into NiO and SiO_2 .

CARBONYL PROCESSES GENERAL

FORMATION OR PREPARATION OF CARBONYLS

536. BADISCHE ANILIN- U. SODA-FABRIK. [Cobalt Carbonyl.] French Patent 33,951, Aug. 1, 1927 (addition to French Patent 607,134); Chem. Abs., vol. 23, 1929, p. 4783¹.

537. CIBA, LTD. Nickel Carbonyl. British Patent 649,988, Feb. 7, 1951 (see Swiss Patent 263,642, Dec. 1, 1949; Chem. Abs., vol. 44, 1950, p. 3682g); Chem. Abs., vol. 45, 1951, p. 6357e.

A good yield (90 to 92 percent) of nickel carbonyl is obtained by introduction of a soluble Ni salt solution, an alkaline reagent, and minor amounts of nickel sulfide or cyanide into a pressure vessel and subjecting to a pressure of 100–130 atmospheres of carbon monoxide at elevated temperatures.

538. COLCLOUGH, T. P. Nickel Production. Metal Ind., vol. 68, No. 21, May 24, 1946, p. 416; Eng. Index, 1946, p. 875. (From Report for Combined Intelligence Objectives Subcommittee.)

Briefly describes the carbonyl process used for production of Ni powder by the I. G. Farbenindustrie, A. G., at Oppau works, Ludwigshaven, Germany.

539. ———. German Iron and Nickel Powders. Iron Age, vol. 157, No. 8, 1946, pp. 48–49; Chem. Abs., vol. 40, 1946, p. 2427⁴.

A report made by the combined intelligence objectives subcommittee on the manufacturing procedures at the Oppau works of the I. G. Farbenindustrie is presented. High-grade Ni and Fe powders were made by the carbonyl process.

540. COMINGS, E. W. Recent Advances in the Use of High Pressures. Ind. Eng. Chem., vol. 39, 1947, pp. 948–952; British Abs., 1948, p. B-1-4.

Reviews literature of the last 5 years dealing with applications of high pressures in industrial chemical processes, with special attention to production of nickel and iron carbonyls in Germany.

541. FISHER, J. W. Regeneration of Nickel Carbonyl (From Aqueous Solutions). British Intelligence Objectives Subcommittee Final Rept. 371, item 22, 4 pp. (see also item 358-B, 1946, p. B-II-311); British Abs., 1946, p. B-I-368.

Waste aqueous NiCl_2 (from syntheses using $\text{Ni}(\text{CO})_4$) is converted into aqueous $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ (4 per cent of Ni in solution); this is treated with CO at 175° C. and 200 atmospheres pressure to yield $\text{Ni}(\text{CO})_4$ smoothly and rapidly.

542. GRESHAM, W. F., AND HARDY, J. V. E. Metallic Carbonyls. U. S. Patent 2,473,993, June 21, 1949; Chem. Abs., vol. 43, 1949, p. 9398b.

CO , H_2 , and a Co or Ni salt of a carboxylic acid at 50 to 1,200 atmospheres and 100°–375° C. temperature give cobalt or nickel carbonyl, which is recovered from the reaction mass at 50°–100° C. by blowing with CO and scrubbing the exit gas with an organic solvent. Outstanding results are obtained at 100–1,000 atmospheres partial pressure of CO, and with an initial H_2 :Ni ratio of 1:1 and 3:1 and an initial CO : H_2 ratio of 25:1 to 500:1. Propionic acid is a suitable solvent for both reaction and recovery.

543. HARRISON, C. F. R., AND WALLIS, A. E. (assigned to International Nickel Co.). Nickel Carbonyl. U. S. Patent 2,167,112, July 25, 1939; Chem. Abs., vol. 33, 1939, p. 8937¹.

Describes a process for the production of nickel carbonyl. The gases containing the condensible nickel carbonyl are cooled to a condensation temperature of 0°–80° C.; and, while the condensation temperature is maintained, the pressure is adjusted by referring to a calculation from the equation ($P=0.6T+22$), liquefying at least 90 percent of the condensible carbonyl, and separating it.

544. I. G. FARBENINDUSTRIE, A. G. Nickel and Cobalt Carbonyls. British Patent 296,558, Sept. 5, 1927; Chem. Abs., vol. 23, 1929, p. 2538¹.

Nickel and cobalt carbonyls are made by the action of CO on the corresponding metals prepared from ammonium compounds, such as are obtained by leaching ores with ammoniacal solution. The pure metals may be obtained from the resulting carbonyls.

545. ———. Cobalt Carbonyl. British Patent 298,714, July 28, 1927; Chem. Abs., vol. 23, 1929, p. 3058¹.

The process of preparing iron carbonyl described in British Patent 250,132 (Chem. Abs., vol. 21, 1927, p. 994) is applied to the preparation of cobalt carbonyl. CO or a gas containing it is passed under pressure over metallic Co (which may be prepared by the reduction of cobalt oxide or cobalt ores with H_2), and the cobalt carbonyl is separated by cooling before releasing the pressure. Gives various details.

546. ———. Cobalt Carbonyl. British Patent 307,112, Dec. 3, 1927 (see Chem. Abs., vol. 23, 1929, p. 3058¹); Chem. Abs., vol. 23, 1929, p. 5281⁶.

In effecting the reaction between Co and CO, oxidizing agents, such as O_2 , CO_2 , or water vapor, are excluded both from the reducing gas used in preparing the metal and from the CO. Treatments for preparing reduced Co and purified CO are described.

547. ———. Carbonyls. British Patent 320,962, Apr. 8, 1932 (see Chem. Abs., vol. 26, 1932, p. 3630¹); Chem. Abs., vol. 27, 1933, p. 3784.

In the production of metal carbonyls (for example, iron or nickel carbonyl) the reaction heat is transferred by conveying a liquid (for example, oils, molten paraffin wax, H_2O , or fused metal carbonyls) through the reaction chamber and bringing it into direct contact with the reaction materials. Alternatively, a gas may be employed, provided it is supplied to, and or withdrawn from, the reaction vessel at several places. The apparatus is described.

548. ———. Metal Carbonyls. British Patent 323,332, Nov. 30, 1928; French Patent 677,548, June 28, 1929 (see Chem. Abs., vol. 24, 1930, p. 2841¹); Chem. Abs., vol. 24, 1930, p. 3329⁷.

Carbonyls of Fe or other metals are formed by action of CO on metals suspended in or made into a paste with a liquid or melt such as paraffin oil, molten paraffin, benzine, and carbonyls of the metal to be converted, at temperatures up to 200° C. and pressures up to 200 atmospheres. Describes various details and modifications of procedure.

549. ———. Metal Carbonyls. British Patent 324,382, Sept. 27, 1928; Chem. Abs., vol. 24, 1930, p. 3329⁸.

Metal for reaction with CO to form metal carbonyl is obtained by reducing oxides, such as those contained in roasted pyrites or oxidic ores, at a temperature above 500° C. (the reduction being effected quickly and the reduced product being cooled quickly, to avoid sintering). H_2 , CO, hydrocarbons, or solid carbonaceous material may be used for the reduction.

550. ———. Extracting Cobalt. British Patent 396,717, Aug. 8, 1933; Chem. Abs., vol. 28, 1934, p. 456⁵.

Cobalt nitrosocarbonyl (1) and/or Co nitrosyl are obtained by acting with NO, if necessary with CO, upon cobalt, or a material containing cobalt as metal or in a state from which it can be reduced to metal

by the reducing gases present such as excess CO. When (1) is produced, the NO may be wholly or in part replaced by substances supplying it (for example, nitrates). Substances (for example, Cu) that facilitate the production of the nitroso compounds may be added. The nitroso compounds may be burned or thermally decomposed in the presence of inert gases, to form CoO, thermally decomposed in the presence of reducing gases (for example, H₂) to form Co, or treated with strong mineral acids to form Co salts. Among examples, an industrial waste containing CoSO₄ and oxides of Fe, Cu, and Co is dried, reduced by H₂ at 380° C., and treated with CO containing NO at 160°–180° C. to produce (1).

551. I. G. FARBENINDUSTRIE, A. G. [Nickel and Cobalt Carbonyls.] French Patent 650,839, Mar. 14, 1928 (see British Patent 296,558; Chem. Abs., vol. 23, 1929, p. 2338); Chem. Abs., vol. 23, 1929, p. 3314².

552. ———. [Metal Carbonyls.] French Patent 679,542, July 30, 1929 (see Chem. Abs., vol. 24, 1930, p. 3329); Chem. Abs., vol. 24, 1930, p. 3865³.

Metal carbonyls are prepared by the rapid reduction of compounds containing metals capable of forming carbonyls, at a temperature above 500° C., followed by a rapid cooling and treatment with CO. Examples are given of the preparation of iron and nickel carbonyls.

553. ———. [Cobalt Nitrosyl.] French Patent 740,095, July 19, 1932; Chem. Abs., vol. 27, 1933, p. 2257.

Cobalt nitrosyl is prepared by treating metallic Co or its compounds with oxides of nitrogen, preferably NO, and preferably under pressure and heat.

554. ———. [Nickel Carbonyl.] French Patent 749,434, July 24, 1933; Chem. Abs., vol. 28, 1934, p. 587⁴.

CO or gases containing it are caused to react, under high pressure, on materials containing Ni and S obtained in a fusion operation. The presence of heavy metals, such as Cu, Fe, or Co, to fix the S is preferred. The product, known as "Ni matte" or "Ni stone," obtained in the manufacture of Ni from its ores may be used.

555. INDUSTRIAL CHEMIST. Nickel Extraction by the Mond Process. Vol. 10, 1934, pp. 253–264; Chem. Abs., vol. 28, 1934, p. 5789⁵.

556. KINCAID, J. F., AND STRONG, J. S. (assigned to Rohm & Haas Co.). Nickel Carbonyl. U. S. Patents 2,548,727 and 2,548,728, Apr. 10, 1951; Chem. Abs., vol. 45, 1951, p. 6357d.

In the first patent a water-soluble Ni salt, such as the chloride or sulfate, is treated with a hydroxide of an alkali or alkaline earth to precipitate nickelous hydroxide, which, after the introduction of a small quantity of a sulfur complex or compound, such as the thiosulfate, is then subjected to a pressure greater than a 1.000 p. s. i. of carbon monoxide. A yield of 99 percent of the possible nickel carbonyl is obtained. In the second patent a cyanide of the alkalies or alkaline earths is substituted for the S complex mixture, with all other conditions unaltered.

557. MAYER, K., AND WIBAUT, J. P. [Preparation of Nickel Tetracarbonyl.] Rec. trav. chim., vol. 56, 1937, pp. 356–358; Chem. Abs., vol. 31, 1937, p. 4918⁶.

Hydrated nickelous oxalate was prepared by treating 300 gm. of Ni(NO₃)₂·2H₂O with 100 gm. of infusorial earth and warm water with 130 gm. of (COOH)₂·2H₂O, filtering, washing, and drying the precipitate at 120° C. to a stiff mass, and then adding 3–4 ml. of concentrated H₂SO₄ and drying until a powder was obtained. A slow stream of CO from HCOOH and H₂SO₄ was passed over a charge of the above precipitate contained in a glass tube heated in a furnace to 450° C. for 1½ hr., and then held at this temperature for 30 minutes. On cooling to 100° C. and passing in a rapid stream of

CO, Ni(CO)₄, separated as a solid in a receiver cooled with a mixture of CO₂ and alcohol.

558. MOND NICKEL CO., LTD. [Nickel Carbonyl.] French Patent 709,381, Jan. 15, 1931; Chem. Abs., vol. 26, 1932, p. 1401.

The speed of formation of Ni(CO)₄ by the action of CO on Ni is increased by the presence in the reaction chamber of a compound containing S, Se, or Te in an "active form." Compounds of S, Se, or Te with Ni are particularly suitable and may be introduced or formed in the reaction chamber. SO₂ may also be used, in which case a temperature of about 330° C. is found suitable. The use of COS, CS₂, and C₂H₄S is also mentioned. The process may be used for extracting Ni from ores.

559. ———. [Nickel Carbonyl.] German Patent 636,534, Oct. 10, 1936; Chem. Abs., vol. 31, 1937, p. 3221⁷.

Describes process for preparing nickel carbonyl by the action of CO on metallic Ni, reduced Ni ores, or ore residues in the absence of O₂ and in the presence of compounds of S, Se, or Te.

560. MOND NICKEL CO., LTD., AND GRIEB, C. M. W. Nickel Carbonyl. British Patent 347,208, Jan. 16, 1930; Chem. Abs., vol. 26, 1932, p. 1725.

In forming nickel carbonyl by passing CO over Ni or in extracting Ni from ores, mattes, etc., in the form of nickel carbonyl, the rate of formation of the latter is increased by the presence of a compound containing S, Se, or Te in "active form." Numerous compounds which may be used and details of procedure are given.

561. MÜLLER, CARL, AND KEUNECKE, EMIL (assigned to I. G. Farbenindustrie, A. G.). [Cobalt Carbonyl.] German Patent 505,211, Aug. 13, 1926 (see British Patent 307,112; Chem. Abs., vol. 23, 1929; p. 5281); Chem. Abs., vol. 24, 1930, p. 5948⁸.

562. MÜLLER, CARL, SCHLECHT, LEO, AND KEUNECKE, EMIL (I. G. Farbenindustrie, A. G.) [Extraction of Carbonyl-Forming Metals From Mixtures of Metals.] German Patent 483,603, Feb. 25, 1927; Chem. Abs., vol. 24, 1930, p. 582⁹.

Iron, Ni, Co, and other carbonyl-forming metals are extracted from mixtures containing other metals by forming the carbonyls at high temperature and high CO pressure. The carbonyls are separated from the starting material and from each other (for example, by fractional distillation or dephlegmation) and decomposed to yield the metals.

563. NAWA, TADASHI, AND KOGURA, SHOICHI (assigned to East Asia Synthetic Chemical Industries Co.). [Continuous Preparation of Nickel Carbonyl.] Japanese Patent 72, Jan. 9, 1953; Chem. Abs., vol. 48, 1954, p. 1642d.

An aqueous solution of Ni(NH₃)₆Cl₂ (250 gm. per l.) at 30° C. and more than the equivalent amount of CO at 190° C. are introduced into a reaction vessel at 140° C. and 300 atmospheres (partial pressure of CO, 80 atmospheres). The product contains Ni(CO)₄, NH₃, and CO₂, which are introduced into a condenser, mixed with 66 percent CO, and cooled at 70° C., and the condensed water is removed. The gas, introduced into a gas-washing tower, is washed with 18 percent NH₄OH to liquefy Ni(CO)₄, and to convert CO₂ into (NH₄)₂CO₃ solution to separate it from CO. The washed liquor is placed in a vessel at 2 atmospheres, and Ni(CO)₄ is drawn off from the bottom layer to give a 91-percent yield at 99-percent purity. The CO is recycled.

564. OHASHI, KUMAO, SUZUKI, SHIGENARI, AND ITO, HIROO (assigned to Toa Gosei Chem. Ind. Co., Nagoya.). [Preparation of Nickel Carbonyl by the Reppe Process. I. Influence of Temperature, Concentration, and Pressure.] Jour. Chem. Soc., Japan

Ind. Chem. Sec., vol. 54, 1951, pp. 454-461; Chem. Abs., vol. 47, 1953, p. 5831g.

For preparing nickel carbonyl from $\text{Ni}(\text{NH}_3)_4\text{Cl}_2$ complex and carbon monoxide, the effects of $\text{Ni}(\text{NH}_3)_4\text{Cl}_2$ concentration, temperature, and pressure were studied. The conditions as given by Reppe with a temperature of about 80°C ., a pressure greater than 50 atmospheres, hold only for a low concentration of the nickel complex.

565. SCHLECHT, LEO, AND NAUMANN, MAX (assigned to I. G. Farbenindustrie, A. G.). [Metal Carbonyls.] German Patent 553,911, July 4, 1930; Chem. Abs., vol. 26, 1932, p. 5710.

In preparing of carbonyls by the action of CO or CO-containing gases on metals, the temperature is regulated by liquids in contact with the reducing materials. Liquids of high specific heat are used. The apparatus is described. Examples describe the preparation of carbonyls of Fe and Ni.

566. — (assigned to I. G. Farbenindustrie, A. G.). [Nickel Carbonyl.] German Patent 571,225, Aug. 8, 1931 (see French Patent 740,408; Chem. Abs., vol. 27, 1933, p. 2257. See British Patent 401,438, Nov. 16, 1933; Chem. Abs., vol. 28, 1934, p. 2476^b); Chem. Abs., vol. 27, 1933, p. 2768.

This deals with the production of carbonyls at pressures of 2 to 1,000 atmospheres and temperatures of 100° - 350°C .

567. — (assigned to I. G. Farbenindustrie, A. G.). [Nickel Carbonyl.] German Patent 618,108, Sept. 2, 1935 (Cl. 12n 4); Chem. Abs., vol. 30, 1936, p. 254².

Metallurgical or other products which contain Ni and S and have been obtained by a process involving fusion, are treated with CO (or gases containing it) at a raised temperature and pressure, for example, 200° - 275°C . and 200 atmospheres, without preliminary roasting and reduction. Good yields of $\text{Ni}(\text{CO})_4$ are obtained. The starting material may be pretreated to increase its surface—for example, by pouring the fused material into water or by granulation. The preferred starting materials contain, in addition to Ni, other heavy metals capable of combining with S, for example, Cu, Co, or Fe. Describes special processes.

568. SCHLECHT, LEO, HAMPRECHT, GÜNTHER, AND SPOUN, FRITZ (assigned to I. G. Farbenindustrie, A. G.). [Cobalt Nitrosocarbonyl.] German Patent 566,448, July 26, 1931; Chem. Abs., vol. 27, 1933, p. 1106.

CO or a gas containing CO is passed over Co or material containing Co in the presence of an oxide of N (for example, NO) or reagents yielding an oxide of N. The reaction may be effected under various conditions, for example, at 60°C . and atmospheric pressure or at 240°C . and 200 atmospheres of pressure. The reaction may be applied to Co ores, scrap, etc., and the carbonyl may be decomposed to give Co or Co compounds.

569. SIMPSON, K. M. Recovery of Nickel Contained in Iron Oxide Ores. U. S. Patent 2,212,459, Aug. 20, 1941 (see Chem. Abs., vol. 34, 1940, p. 5815^a); Chem. Abs., vol. 35, 1941, p. 427^a.

Describes an arrangement of apparatus and a process for recovering substantially pure Ni from iron oxide ores containing relatively low amounts of nickel oxide. The ore is selectively reduced to reduce the major portion of the nickel oxide while the reduction of iron oxide is retarded; the reduced ore is treated with CO at a temperature of 40° - 80°C ., to form gaseous nickel carbonyl containing a relatively small amount of gaseous iron carbonyl, the iron carbonyl is separated from the nickel carbonyl by dissolving and distillation, and the nickel carbonyl is decomposed to produce substantially pure Ni.

570. SUZUKI, SHIGENARI, AND ITO, HIROO (assigned to East Asia Synthetic Chemical Industry Co.). [Nickel Carbonyl From a Complex Nickel-Ammonium Salt.] Japanese Patent 2,230, May 8, 1951; Chem. Abs., vol. 47, 1953, p. 839a.

A 95-percent yield of nickel carbonyl was obtained in 4 hours from 300 grams of the Ni complex, $\text{Ni}(\text{NH}_3)_4\text{Cl}_2$, with 400 gm. of water at an autoclave pressure of 100 kg. per cm^2 with CO gas at 160°C .

571. URAZOVSKII, S. S. [The Preparation of Metal Carbonyls.] Jour. Chem. Ind. (Moscow), No. 5, 1932, pp. 23-28; Chem. Abs., vol. 26, 1932, p. 5269.

The optimum conditions for preparing $\text{Ni}(\text{CO})_4$ at atmospheric pressure are the passage of CO over Ni, freshly reduced on pumice, at the rate of 1.5 l. per min. at 45° - 50°C . The presence of rubber in the apparatus causes easy decomposition of the product.

572. WATSON, K. M. (assigned to Sinclair Refining Co.). Concentrating or Purifying Carbon Monoxide Occurring in Admixture With Other Gases. U. S. Patent 2,593,232, Apr. 15, 1952; Chem. Abs., vol. 46, 1952, p. 5823g.

Carbon monoxide is recovered from admixture with other gases by treating with Ni in a form having a high surface area at 40° - 200°C . and pressures up to 100 p. s. i. to form nickel carbonyl. The Ni may be advantageously supported on kieselguhr and used in granular or pelleted form or in a fluidized bed. The mass containing nickel carbonyl is then passed through a vessel at 100° - 400°C . or higher at pressures up to 100 p. s. i., where CO is released and Ni is restored to its metallic form. Higher temperatures are always used in the decomposition step than in the absorption step. The mass containing Ni is then cooled to the approximate temperature of the absorption vessel and reused to absorb CO.

573. YAMAMOTO, KAZUMI, AND SATO, KAZUTOSHI (assigned to Mitsui Chemical Industries Co.). [Preparation of Cobalt Carbonyl.] Japanese Patent 985, Mar. 9, 1953; Chem. Abs., vol. 48, 1954, p. 2996f.

Ten parts of CoCl_2 in 50 parts of water and 2.5 parts of kieselguhr is treated at 60°C . with 13 parts of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ in 30 parts of water. The precipitate is filtered, washed, and dried, treated with 5 parts of 5-percent H_2SO_4 , and dried to give a product containing 2.3 parts of Co and 0.02 part of S. The product is reduced in H_2 at 400°C ., cooled, placed in an autoclave with CO at 100 atmospheres, and heated for 2 hr. at 120°C .; the product is extracted with Et_2O to give 92-percent cobalt carbonyl.

FRACTIONAL DISTILLATION OF CARBONYLS AND SEPARATIONS

574. HARRISON, C. F. R., AND WALLIS, A. E. Nickel Carbonyl. British Patent 426,741, Apr. 9, 1935; Chem. Abs., vol. 29, 1935, p. 6374^a.

Nickel carbonyl in the liquid phase is separated from a mixture of gases or vapors containing CO and $\text{Ni}(\text{CO})_4$ at a partial pressure of CO such that the vapor pressure of $\text{Ni}(\text{CO})_4$ is near a minimum for the condensation temperature.

575. —. Purifying Crude Nickel Carbonyl. British Patent 428,610, May 13, 1935; Chem. Abs., vol. 29, 1935, p. 7028¹.

The purity of nickel carbonyl may be increased by a temperature treatment in which the nickel carbonyl is lowered below its melting point, while still above the freezing point of the impurity, and separating by decanting; an agent, such as water, may be added to trap suspended matter on freezing.

576. MOND NICKEL CO., LTD. [Nickel Carbonyl.] French Patent 781,133, May 9, 1935; Chem. Abs., vol. 29, 1935, p. 6374⁹.

The separation of liquid nickel carbonyl from a mixture of gases and vapors in a condensation vessel is detailed. The partial pressure of CO is adjusted to be near a maximum with respect to the total pressures of CO and nickel carbonyl.

577. MÜLLER, CARL, SCHLECHT, LEO, AND KEUNECKE, EMIL (assigned to I. G. Farbenindustrie, A. G.). Separating Carbonyl-Forming Metals, Such as Iron, Nickel, Cobalt, etc. U. S. Patent 2,004,534, June 11, 1935; Chem. Abs., vol. 29, 1935, p. 5062³.

CO is caused to react with material containing metals to form carbonyl compounds of the metals to be separated, and the carbonyl mixture is fractionated. Gives numerous examples, with details.

578. YOUNG, R. S. (assigned to International Nickel Co. of Canada, Ltd., New York, N. Y.). Purification of Nickel With Carbonyl. Jour. Chem. Educ., vol. 31, 1954, p. 26; Chem. Abs., vol. 48, 1954, p. 4900e.

A demonstration experiment is described to reproduce on a laboratory scale a commercial process by which Ni is refined. Ni is isolated and purified by means of carbonyl. A demonstration illustrates gas-solid reactions of oxide reductions, low-temperature volatilization of a metal, dissociation of a gas (at slightly higher temperatures) into a metal and another gas, and catalysis. The equipment described is simple, only atmospheric pressure is required, and the temperatures are relatively low.

DECOMPOSITION OF CARBONYLS

579. HUNAKOSHI, SHIGEO (assigned to Nippon Kôgyô K. K.). [Refining Nickel.] Japanese Patent 109,489, Feb. 5, 1935; Chem. Abs., vol. 29, 1935, p. 4318⁶.

Fine particles of Ni obtained by heating nickel carbonyl are gathered in a Cottrell dust collector.

580. MOND NICKEL CO., LTD., AND WALLIS, A. E. Decomposition of Nickel Carbonyl. British Patent 620,287, Jan. 15, 1947. British Abs., 1950, p. B-1-120.

Nickel pellets, preheated to above the decomposition temperature of Ni(CO)₄, are passed downward through a vertical decomposer countercurrent to Ni(CO)₄ introduced at the bottom.

581. MÜLLER, CARL, AND SCHUBARDT, WALTER (assigned to I. G. Farbenindustrie, A. G.). Pure Metal From Carbonyls. U. S. Patent 1,759,661, May 20, 1930; Chem. Abs., vol. 24, 1930, p. 3480.

Carbonyls of metals having an atomic weight higher than 56, such as those of Ni, Co, and Mo, are decomposed in the manner described for Fe in United States Patent 1,759,659 (preceding abstract). The apparatus is described. The patent referred to above specifies decomposing iron carbonyl in the hot free space of a heated vessel some distance from its walls.

582. — (assigned to I. G. Farbenindustrie, A. G.). [Pure Metals.] German Patent 511,564, July 7, 1926 (addition to German Patent 500,692; Chem. Abs., vol. 25, 1931, p. 481) (see Chem. Abs., vol. 24, 1930, p. 3480); Chem. Abs., vol. 25, 1931, p. 1211⁴.

The method described in German Patent 500,564 for preparing pure Fe by the thermic decomposition of Fe(CO)₅ is extended to other metals. Cobalt tetracarbonyl alone or mixed with Fe(CO)₅ is heated in a current of indifferent gas or vapor to produce Co, or Co+Fe. The carbonyls of Ni and Co may be similarly decomposed.

583. STANDARD OIL DEVELOPMENT CO. Recovery of Cobalt Carbonyl in the Synthesis of Oxygenated Or-

ganic Compounds. British Patent 670,898, Jan. 20, 1950; U. S. Patent Nov. 4, 1949; British Abs., 1952, p. B-1-1214.

In the carbonylation of olefins with CO and H₂ in the presence of a Co catalyst, cobalt carbonyl is removed from the liquid product by passing it into contact with a hot rotating surface, preferably kept at 300°-350° F., and from which the metallic Co is continuously scraped.

584. WALLIS, A. E. (assigned to Mond Nickel Co.). Decomposition of Nickel Carbonyl. British Patent 620,287, Mar. 22, 1949; Chem. Abs., vol. 43, 1949, p. 7204a; vol. 44, 1950, p. 528d.

In the production of Ni, Ni pellets at 220°-240° C. initially are passed countercurrent to gases containing 4 percent or more Ni(CO)₄, and the pellet temperature is allowed to drop to 140°-160° C. at the Ni(CO)₄ inlet. Thus pellets at the highest temperatures come into contact only with Ni(CO)₄ of low concentration, and C deposition is prevented.

MATTES AND METALLURGICAL PRODUCTS

585. BADISCHE ANILIN- U. SODA-FABRIK (assigned to I. G. Farbenindustrie, A. G., in Auflösung). Nickel-Copper Matte. British Patent 702,011, Jan. 6, 1954; Chem. Abs., vol. 48, 1954, p. 7527d.

For complete removal of Fe from Ni-Cu matte, the S content must be lowered so much that not enough is left behind to bind all the Cu and Ni as sulfides. If this product is subjected to an annealing treatment, fine grinding, and magnetic separation, a portion of the Cu and Ni is removed in the form of metallic crystallites, which contain most of the precious metals of the original matte. By subjecting the metallic part to a treatment with CO at 200 atmospheres pressure and 200°-230° C. temperature, Ni is almost completely removed as nickel carbonyl.

586. CHARLSON, T. S., DAVEY, T. H., AND PFEIL, L. B. Nickel and Iron Powder Plants of I. G. Farbenindustrie Oppau Works, Ludwigshafen. (B) Treatment of Nickel-Copper Ores and Residues at Nord-deutsche Affinerie, Hamburg. Intelligence Objectives Subcommittee Final Rept. 263, item 21, 1946, 17 pp.; British Abs., 1946, p. B-1-303.

(A) Crushed Ni matte, smelted from Petsamo ore, was treated with CO under pressure to produce liquid Ni(CO)₄, from which the Ni powder was produced by normal decomposition after purification by distillation.

(B) Petsamo Ni ore was smelted in blast furnaces, and the low-grade matte produced was treated in the converter. Residues after extraction of Ni at Oppau were combined with other Cu concentrate passing through the process.

587. GARRATT, A. P., AND THOMPSON, H. W. Thermal Decomposition and Oxidation of Nickel Carbonyl. Jour. Chem. Soc., 1934, pp. 1822-1825 (see Chem. Abs., vol. 29, 1935, p. 1713⁴); Chem. Abs., vol. 29, 1935, p. 1702¹.

Glass vessels of various dimensions were used in studying the decomposition of nickel carbonyl and its oxidation in the temperature range from 0°-100° C. Pressure changes were indicated on a manometer. Thermal decomposition without the addition of oxygen was slight. Decompositions with O₂, if they occurred at all, were explosive. The thermal decompositions showed that initially, at 100° F., the rate of decomposition varied with the first power of the concentration, but in later stages CO had a retarding effect. The Arrhenius energy of activation is 12,000 calories. Thermal decomposition agrees with the reaction: (1) Ni(CO)₄ → Ni(CO)₂ + CO, (2) NiCO₂ → Ni + 3CO, and (3) Ni(CO)₂ + CO → Ni(CO)₄.

588. GRIEB, C. M. W. (assigned to International Nickel Co.). Nickel Carbonyl. U. S. Patent 1,909,762, May 16, 1933; Chem. Abs., vol. 27, 1933, p. 3786.

In extracting Ni from ores, residues, mattes, and the like, nickel carbonyl is formed from reduced Ni and CO in a reaction chamber, and the rate of formation of nickel carbonyl is increased by carrying out the reaction in the absence of O_2 and in the presence of a compound containing a member of the S group in active form, such as a sulfide.

589. HARRISON, C. F. R., AND WALLIS, A. E. Nickel Carbonyl, Extracting Metals. British Patent 429,274, May 28, 1935 (see Chem. Abs., vol. 29, 1935, p. 6374⁵); Chem. Abs., vol. 29, 1935, p. 7027⁵.

Nickel tetracarbonyl is made by the action of CO under pressure on Ni matte mechanically mixed, without fusion, with Cu or Fe in sufficient amount for all the S to be bound as cuprous or iron sulfide. The Cu or Fe may be added as such or as oxides, in which case the mixture is reduced before the CO treatment, or as calcined or calcined and reduced mattes or as residues from the treatment. In the last case, the same Cu and Fe may be used repeatedly until a large enough quantity of precious metals has accumulated to be recovered. Examples are given.

590. ——— (assigned to International Nickel Co., Inc.). Nickel Carbonyl. Canadian Patent 357,449, Apr. 28, 1936; Chem. Abs., vol. 30, 1936, p. 4278⁵.

Nickel carbonyl is prepared by treating Ni matte or similar material with CO under pressure. For example, a mixture of nickel sulfide matte and Cu is moistened with H_2O equal to 5 percent of the weight of the powder. The damp mixture is pressed into 20-gm. briquets under a pressure of 10 tons per sq. in. and dried at 60° C. for 20 hr. About 90 percent of the Ni can then be extracted by about 10 hr. of treatment with CO.

591. ——— (assigned to International Nickel Co.). Nickel Carbonyl. U. S. Patent 2,070,079, Feb. 9, 1937; Canadian Patent 363,831, Feb. 2, 1937; Chem. Abs., vol. 31, 1937, p. 2369⁵.

The pulverized Ni matte is mixed with finely divided Cu or Fe in a small amount of H_2SO_4 to act as binder in briquetting and also aid in carbonyl formation; CO under pressure is passed through the briquets to extract substantially all of the Ni.

592. ——— (assigned to International Nickel Co.). Nickel Carbonyl. U. S. Patent 2,105,037, Jan. 11, 1938 (see Chem. Abs., vol. 31, 1937, p. 2369⁵); Chem. Abs., vol. 32, 1938, p. 2301.

An unfused mixture of Ni matte with separated particles of iron or copper sulfides in the fine division is subjected to the action of CO under pressure to facilitate separation of Ni from the residue. The residue is calcined to remove substantially all the S of the sulfides, and the calcined residue is used in the first step of the process to effect concentration of precious metals in the Ni matte.

593. I. G. FARBENINDUSTRIE, A. G. Nickel and Iron Carbonyls. British Patent 394,906, July 6, 1933 (see Chem. Abs., vol. 27, 1933, p. 2257); Chem. Abs., vol. 28, 1934, p. 267⁵.

Nickel tetracarbonyl is obtained by acting directly with CO-containing gases, such as producer, water, or illuminating gas, at elevated temperature and pressure on Ni-containing mattes or stones or like products. They may contain Ni and S, with or without other metals, such as noble metals or heavy base metals that combine with S (for example, Fe, Co, Cu, and Mo). The gases may be led in a cycle, impurities such as COS being removed and CO regenerated therefrom. The initial materials may be treated to enlarge their surface before the reaction—for example, given a blis-

tered or foamy structure, granulated by pouring into water, etc. If Fe is present, the reaction may be so conducted that Ni only is attached or that mixtures of carbonyls may be obtained that may be subsequently separated. Impure Ni may be refined by fusing with NiS, FeS, other sulfides, or S and subjecting the resulting matte to CO action.

594. ———. Nickel. British Patent 509,076, July 11, 1939; French Patent 852,322, Jan. 30, 1940; Chem. Abs., vol. 36, 1942, p. 1890⁵; vol. 34, 1940, p. 2777⁵.

Crude nickel carbonyl, which has previously been purified to contain at most only 0.1 percent Fe, is subjected to thermal decomposition to produce a low-carbon Ni.

595. ———. [Nickel Carbonyl.] French Patent 851,076, Jan. 2, 1940 (see U. S. Patent 2,245,503; Chem. Abs., vol. 35, 1941, p. 6073⁵); Chem. Abs., vol. 36, 1942, p. 2006⁵.

596. MANCHOT, WILHELM, AND GALL, HEINRICH. [Nickel Carbonyl.] German Patent 577,144, May 24, 1933; Chem. Abs., vol. 27, 1933, p. 4036.

An aqueous suspension of NiS or $Ni(SH)_2$, obtained by treating a nickel-salt solution with H_2S or a sulfide, is treated with CO at atmospheric temperature and pressure. Nickel carbonyl is recovered in a known manner from the gaseous reaction products. The process may be used in separating Ni from Co, etc. Examples are given.

597. MOND NICKEL CO., LTD. [Nickel Carbonyl.] French Patents 781,619 and 781,620, May 18, 1935; Chem. Abs., vol. 29, 1935, p. 6375⁵.

In the first patent, Fe or Cu is added to the Ni matte by mechanical mixing without fusion and subjected to carbon monoxide under pressure; then the residue is reduced and recycled with a fresh matte. In the second patent, the powdered matte is mixed with Cu or Fe in finely divided condition, water or other binder is added, and the material is made into balls, which are subjected to CO under pressure.

598. ———. [Nickel Carbonyl.] German Patent 671,007, Jan. 31, 1939 (Cl. 12n 4) (see British Patent 429,274; Chem. Abs., vol. 29, 1935, p. 7027⁵); Chem. Abs., vol. 33, 1939, p. 3545⁵.

599. MOND NICKEL CO., LTD., AND WALLIS, A. E. Nickel Carbonyl. British Patent 481,511, Mar. 9, 1938; Chem. Abs., vol. 32, 1938, p. 6812⁵.

Material suitable for preparing $Ni(CO)_4$ by direct treatment with CO under pressure is obtained by reducing a sintered Ni matte by heating it with a solid or liquid carbonaceous material, such as coke, coal, anthracite, or heavy oil.

The matte may be obtained by passing "2d bottoms" from the Orford "tops-and-bottoms" process through a sintering machine.

600. SCHLECHT, LEO, AND HAMPRECHT, GÜNTHER. [Pure Metal Carbonyls.] German Patent 654,558, Dec. 24, 1937 (Cl. 12n 1) (see French Patent 809,545; Chem. Abs., vol. 31, 1937, p. 8842⁵); Chem. Abs., vol. 32, 1938, p. 3560⁵.

601. SCHLECHT, LEO, AND NAUMANN, MAX (assigned to I. G. Farbenindustrie, A. G.). Nickel and Iron Carbonyls. U. S. Patent 2,086,881, July 13, 1937; Chem. Abs., vol. 31, 1937, p. 6425⁵.

The reaction is effected at about 50° C. and a pressure of at least 20 atmospheres between carbon monoxide and matte containing 5 to 30 percent in original sulfur and containing at least 1 of the metals Fe or Ni.

602. SCHLECHT, LEO KLIPPEL, H., AND STAEGER, R. (assigned to I. G. Farbenindustrie, A. G.). [Nickel Carbonyl.] German Patent 703,566, Feb. 6, 1941 (Cl. 12n 4) (see U. S. Patent 2,245,503; Chem. Abs., vol. 35, 1941, p. 6073⁵); Chem. Abs., vol. 36, 1942, p. 230⁵.

603. SCHLECHT, LEO, STAEGER, RUDOLPH, AND KLIPPEL, HERMANN (assigned to I. G. Farbenindustrie, A. G.). Nickel Carbonyl Production. U. S. Patent 2,245,503, June 10, 1941; Chem. Abs., vol. 35, 1941, p. 6073^o.

A nickel matte containing at least some Fe or Cu is roasted to remove excess S over that necessary to combine with the metals. The partly roasted product is reduced with H₂ under pressure and then carbonyled by treatment with CO.

604. WALLIS, A. E. (assigned to International Nickel Co.). Nickel Carbonyl. U. S. Patent 2,159,412, May 23, 1939; Chem. Abs., vol. 33, 1939, p. 7057².

A material suitable for treating with CO under 20 to 50 atmospheres and at temperatures of 70°–120° C. to produce nickel carbonyl is described. The Ni matte is sintered in the presence of O₂ to yield a granular product, mixed with a carbonaceous reducing agent, and reduced. The resulting material may be stored in air without materially affecting its carbonyl yield.

605. WINDSOR, M. M., AND BLANCHARD, A. A. Nickel Carbonyl—Mechanism of Its Formation From Nickel Sulfide and Carbon Monoxide. Jour. Am. Chem. Soc., vol. 55, 1933, pp. 1877–1883; Chem. Abs., vol. 27, 1933, p. 3416.

The suspension of NaOH 1, Na₂S 0.1, and NiSO₄ 0.5 mole per liter in the presence of CO gas produces the optimum yield of Ni(CO)₄. Nickel tetracarbonyl may also be formed by the dissociation of NiS or NiSe in the presence of an S-removing agent and CO.

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The advantages accruing from the application of crystal-structure data to the chemistry of the solid state are discussed.

607. BAHR, H. A., AND JESSEN, V. [Dissociation of Carbon Monoxide on Cobalt.] Ber. Deut. chem. Gesell., vol. 63B, 1930, pp. 2226–2237; Chem. Abs., vol. 25, 1931, p. 22².

608. BIBRING, HERVÉ, AND SEBILLEAU, FRANÇOIS. [The Allotropic Transformation of Cobalt.] Compt. rend., vol. 239, 1954, pp. 54–56; Chem. Abs., vol. 49, 1955, p. 6881.

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This note supplements a recent paper by Powell (Chem. Abs., vol. 25, 1931, p. 873⁸), which presented a study of the deviation of direction of the effective magnetizing field in single crystals of Fe, Ni, and Co from the direction of holomagnetization in terms of the (*l*, *s*) interaction between the spins of the pivoting

magnetic electrons and the nonpivoting orbital momentum of the atoms.

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Nickel element (p. 34). The calculation of entropy was based entirely on the data of Eucken and Werth, with the result $S_{298.1}=7.12\pm0.1$.

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674. BOYLE, B. J., KING, E. G., AND CONWAY, K. C. (Bureau of Mines, Berkeley, Calif.). Heats of Formation of Nickel and Cobalt Oxides (NiO and CoO) by Combustion Calorimetry. *Jour. Am. Chem. Soc.*, vol. 76, 1954, pp. 3835-3837; *Chem. Abs.*, vol. 48, 1954, p. 13,397i.
675. BREWER, LEO, AND MASTICK, D. F. The Stability of Gaseous Nickel Oxide. U. C. R. L. Paper 532—Technical Information Division, O. R. E., Oak Ridge, Tenn. A. E. C., Oak Ridge, Tenn., Feb. 7, 1950, unclassified. U. S. Government Publications Monthly Catalog, 1950, Superintendent of Documents, item 8864.
676. CHUFAROV, G. I., ZHURAVLEVA, M. G., AND TATIEVSKAYA, E. P. (Institute of Chemistry and Metallurgy Ural Branch Academy of Sciences, U. S. S. R.). [Reduction and Dissociation of Oxides of Cobalt and Nickel.] *Sverdlovsk. Doklady Akad. Nauk, S. S. S. R.*, vol. 73, 1950, pp. 1209-1212; *Chem. Abs.*, vol. 45, 1951, p. 426i.
677. DIEV, N. P., AND GRIBOVSKII, V. V. [Cobalt Silicates—Synthetic.] *Jour. Appl. Chem., U. S. S. R.*, vol. 18, 1945, pp. 181-183; *Chem. Abs.*, vol. 39, 1945, p. 5193⁸.
- In the system CoO-SiO_2 only the cobalt orthosilicate, $2\text{CoO} \cdot \text{SiO}_2$, can be obtained by heating. The lattice dimensions and type are near those of $2\text{FeO} \cdot \text{SiO}_2$; this indicates that there is mutual isomorphic replacement of oxides of Co and Fe in the silicates of converter slag.
678. EMMETT, P. H., AND SCHULTZ, J. F. Equilibrium in the System: Carbon Monoxide-Water-Cobalt Oxide-Hydrogen. Free-Energy Changes for the Reaction $\text{Co} + \frac{1}{2}\text{O}_2 = \text{CoO}$. *Jour. Am. Chem. Soc.*, vol. 51, 1929, pp. 3249-3262; *Chem. Abs.*, vol. 24, 1930, p. 774².
679. ———. Equilibrium in the System $\text{Co-CO}_2\text{-CoO-CO}$, Indirect Calculation of the Water-Gas Equilibrium Constant. *Jour. Am. Chem. Soc.*, vol. 52, 1930, pp. 1782-1793; *Chem. Abs.*, vol. 24, 1930, p. 3157⁴.
680. GORALEVICH, D. K. [Higher Oxygen Compounds of the Eighth Group of the Periodic System. II. Compounds of Nickel. III. Nickel Oxides.] *Jour. Russian Phys. Chem. Soc.*, vol. 62, 1930, pp. 1165-1188 (see *Chem. Abs.*, vol. 22, 1928, p. 1294); *Chem. Abs.*, vol. 29, 1931, pp. 655 and 2931.
- The preparation and properties of the compounds K_2NiO_4 , Na_2NiO_4 , BaNiO_5 , Na_2NiO_5 , K_2NiO_5 , and Ni_2O_5 are described. A white, unstable oxide NiO , can be formed, which, however, decomposes in air into NiO and O_2 .
- Among the oxides, good evidence is found for the existence of NiO , Ni_2O_3 , Ni_3O_4 , and NiO_2 . Of more doubtful existence are Ni_5O_{10} , Ni_6O_{11} , Ni_7O_{12} , Ni_8O_{13} , Ni_9O_{14} , $\text{Ni}_{10}\text{O}_{15}$, and $\text{Ni}_{11}\text{O}_{16}$.
681. HEDVALL, J. A., AND SCHILLER, G. [The Increased Velocity of Formation of Silicates in Powdered Mixtures as a Result of the Opening up of the Metallic Oxide and Crystallographic Transformation of Quartz.] *Ztschr. anorg. allgem. Chem.*, vol. 221, 1934, pp. 97-102; *Chem. Abs.*, vol. 29, 1935, p. 2430¹.
- In a transitional state many minerals are highly reactive, and the otherwise very inert SiO_2 is no exception to this fact, particularly if the quartz lattice is experiencing the change from alpha-quartz to cristobalite at about 870° C. The reactions between SiO_2 and ZnO , CuO , NiO , CoO , and Co_3O_4 are studied under these conditions. Although ZnO , NiO , and CuO show markedly increased activity at 870° C., the effect is very much greater with cobalt oxides. This is attributed to the incompletely formed lattice of the mixed oxide Co_3O_4 .
682. HENDRICKS, S. B., AND ALBRECHT, W. H. (Rockefeller Institute, New York). [X-ray and Chemical Investigation of Various Oxides of Iron and Cobalt.] *Ber. Deut. chem. Gesell.*, vol. 61B, 1928, pp. 2153-2161; *Chem. Abs.*, vol. 23, 1929, p. 1030².
- Co_3O_4 shows by X-ray analysis the same crystal structure as Fe_3O_4 , although the atomic distances in Co_3O_4 are somewhat smaller.
683. HEYMANN, T., AND JELLINEK, K. [Equilibrium of $\text{Ni} + \text{Co}^{++} \rightleftharpoons \text{Ni}^{++} + \text{Co}$ and Normal Electrode Potential of Cobalt.] *Ztschr. physikal. Chem.*, vol. A160, 1932, pp. 34-38; *Chem. Abs.*, vol. 26, 1932, p. 3983.
684. HOLGERSSON, SVEN, AND KARLSSON, ALDO. [X-ray Examination of Mixed Crystals With Monoxide Components.] *Ztschr. anorg. allgem. Chem.*, vol. 182, 1929, pp. 255-271; *Chem. Abs.*, vol. 23, 1929, p. 5372.
- In the systems CoO-MgO , NiO-MgO , and CoO-NiO a continuous miscibility is observed.
685. HULDT, L., AND LAGERQVIST, A. (University of Stockholm). [The Dissociation Energy of Gaseous Nickel Oxide.] *Ztschr. Naturforsch.*, vol. 9a, 1954, pp. 358-359 (see *Chem. Abs.*, vol. 45, 1951, p. 404e; vol. 47, 1953, p. 937e; and vol. 48, 1954, p. 5636i); *Chem. Abs.*, vol. 49, 1955, p. 9132f.
686. IIDA, SHUICHI (Tokyo University). [Formation Energy of the Superlattice in Ni_3Fe . II. Kinetics of the Superlattice in the Stage of Local Ordering.] *Jour. Phys. Soc., Japan*, vol. 9, 1954, pp. 346-354 (see *Chem. Abs.*, vol. 47, 1953, p. 6212b); *Chem. Abs.*, vol. 48, 1954, p. 13,378a.
- In the composition range from 40 to 100 percent Ni, the binary Fe-Ni alloys form continuous solid solutions, with face-centered cubic crystals, of which the superlattice Ni_3Fe is a member.
687. JANDER, WILHELM, AND SENE, HANS. [The Equilibrium $\text{FeO} + \text{Ni} \rightleftharpoons \text{NiO} + \text{Fe}$ in Liquid Condition.] *Ztschr. anorg. allgem. Chem.*, vol. 210, 1933, pp. 316-324; *Chem. Abs.*, vol. 27, 1933, p. 2368.
- The equilibrium was studied between 1,550° and 1,800° C. At 1,600° C., if the molecular concentration of Ni in the slag is plotted against Ni in the metal phase, a hyperbola results. The equilibrium constant K_H fluctuates around 0.0128, and the reaction therefore obeys the ideal mass-reaction law.
688. ———. [Dependence of the Equilibrium $\text{FeO} + \text{Ni} \rightleftharpoons \text{NiO} + \text{Fe}$ in the Melt on Added SiO_2 . III. Equilibrium Between Metals, Oxides, and Silicates in the Melt.] *Ztschr. anorg. Chem.*, vol. 217, 1934, pp. 48-52 (see *British Chem. Abs.*, 1933, p. A-352); *British Chem. Abs.*, 1934, p. A-365.
- In the presence of SiO_2 up to 12 percent, the value of $K = (\text{Fe})(\text{NiO})/(\text{Ni})(\text{FeO})$ at 1,600° C. diminishes, if no distinction is made between combined and uncombined oxide; this indicates that $\text{FeO} \cdot \text{SiO}_2$ undergoes less dissociation than $\text{NiO} \cdot \text{SiO}_2$, or, alternatively, that the solvent has changed the activity of the molecules. The dependence of K on temperature in the presence of SiO_2 is represented by $\log K = -6,300/T + 1.29$.
689. JEFFERSON, M. E., AND SCHULTZ, J. F. Some Observations on the Oxides of Nickel. *Ztschr. Krist.*, vol. 73, 1930, pp. 376-380 (in English); *Chem. Abs.*, vol. 24, 1930, p. 4438⁷.
- X-ray data indicate the following transition temperatures for Co: Hexagonal close-packed $\rightarrow$ cubic close-

packed ($400^{\circ}\text{C} \pm 20^{\circ}\text{C}.$) $\rightarrow$ hexagonal close-packed ($1,015^{\circ}\text{C} \pm 20^{\circ}\text{C}.$).

690. KAPUSTINSKII, A. F., AND GOFMAN, E. [Equilibrium of the Reaction $\text{Co} + \text{CO}_2 = \text{CoO} + \text{CO}$.] *Acta physicochim.*, U. R. S. S., vol. 6, 1937, pp. 487-490; *British Abs.*, 1937, p. A-I-516.

Equilibrium data for this reaction have been determined for the temperature range 720° - $1,120^{\circ}\text{C}.$ by the method previously described (*British Chem. Abs.*, 1936, p. A-1464, and 1937, p. A-137). The heat of formation of CoO is 53,408 gm.-calories per mole and the change in free energy at $25^{\circ}\text{C}.$ is 11,400 gm. calories per mole.

691. ———. [Equilibrium in the Reduction of Cobalt Oxide by Carbon Monoxide.] *Jour. Phys. Chem.*, U. S. S. R., vol. 9, 1937, pp. 713-715; *Chem. Abs.*, vol. 31, 1937, p. 8329⁶.

Equilibrium in the reduction of cobalt oxide by CO was investigated.

692. KAPUSTINSKII, A., AND SHAMOVSKII, L. [A Method for the Direct Determination of the Dissociation Pressure of Metallic Oxides.] *Ztschr. anorg. allgem. Chem.*, vol. 216, 1933, pp. 10-16; *Chem. Abs.*, vol. 28, 1934, p. 1251⁸.

693. KAPUSTINSKII, A. F., AND ZIL'BERMAN, A. [Equilibrium of Reaction of Nickel With Carbon Dioxide.] *Acta physicochim.*, U. R. S. S., vol. 5, 1936, pp. 605-616; *Chem. Abs.*, vol. 31, 1937, p. 7349⁸.

Equilibrium data for $\text{Ni} + \text{CO}_2 = \text{NiO} + \text{CO}$ have been determined by the method previously described (*Chem. Abs.*, vol. 31, 1937, p. 5729⁸), between 600° and $1,000^{\circ}\text{C}.$ The heat of formation, free energy, and entropy of NiO are calculated.

694. KELLEY, K. K. *Thermodynamic Data on CoSO_4 ; Contributions to the Data on Theoretical Metallurgy.* Bureau of Mines Bull. 406, 1937, 154 pp.

695. ———. *Thermodynamic Data on NiSO_4 ; Contributions to the Data on Theoretical Metallurgy.* Bureau of Mines Bull. 406, 1937, 154 pp.

696. KELLEY, K. K., AND ANDERSON, C. T. *Heat and Free Energies of Formation and of Decomposition of Cobalt Carbonate; Contributions to the Data on Theoretical Metallurgy.* Bureau of Mines Bull. 384, 1935, 73 pp.

697. ———. *Nickel Carbonate and Cobalt Carbonate; Contributions to the Data on Theoretical Metallurgy.* Bureau of Mines Bull. 384, 1935, 73 pp.

698. KLEPPA, O. J. [The Equilibrium $\text{CoO} + \text{H}_2 = \text{Co} + \text{H}_2\text{O}$. The Molar Entropy of Cobaltic Oxide.] *Svensk Kem. Tid.*, vol. 55, 1943, pp. 18-25; *Chem. Zentralbl.*, vol. I, 1943, p. 1970; *Chem. Abs.*, vol. 38, 1944, p. 4855⁹.

The equilibrium was studied by the stream method, and values were obtained that agree with the static method. For the constant $K_p = p_{\text{H}_2\text{O}}/p_{\text{H}_2}$, the heterogeneous equilibrium gives $K_{p_{600}} = 39.35$, $K_{p_{700}} = 44.2$, $K_{p_{750}} = 51.3$, and $K_{p_{800}} = 56.8$ (temperatures in degrees Kelvin). According to $\Delta F = -RT \log K_p$, the change in free enthalpy (reaction work) can be calculated and also the heat content by means of Van't Hoff's equation, which can then be determined at other temperatures with the help of molecular heat. The normal values $\Delta F_{298}^{\circ} = -3,461$ cal. per mol., and $W_{p_{298}} = 859$ cal. per mol. are obtained, from which it follows that $\Delta S_{298}^{\circ} = 8.73$ cal. per mol. per degree. From the known normal entropies of H_2O , Co , and H_2 , it follows that $S_{298}^{\circ} \text{Co} = 11.94 \pm 0.2$ cal. per deg. mol.

699. LEBEDEV, B. G. [The Reducibility of the Oxides of Cobalt.] *Sbornik Khim. i. Term. Met. Obrab. Stali*, 1938, pp. 178-203; *Khim. Referat, Zhur.*, vol. I, No. 11-12, 1938, pp. 39-40; *Chem. Abs.*, vol. 33, 1939, p. 8089⁸.

The compositions of gas phases in equilibrium with Co oxides and their reduction products were investigated. At a strictly constant temperature the same portion of CO was passed repeatedly over the solid phase. From a study of the reaction $\text{CoO} + \text{CO} = \text{Co} + \text{CO}_2$, a number of values were obtained for the composition of the gas phase at 798° - $1,082^{\circ}\text{C}.$; a curve is given of the relation between the temperature and the log of the equilibrium constant. The results obtained compare favorably with those obtained by other investigators. Cobalto-cobaltic oxide has high dissociation pressure and evolves O_2 on heating.

700. LEBLANC, M., AND MÖBIUS, E. [Studies on Cobalt Oxides and Their Systems With Oxygen.] *Ztschr. physik. Chem.*, Abt. A, vol. 142, 1929, pp. 151-176; *Chem. Abs.*, vol. 23, 1929, p. 4417².

701. LUBOJATSKY, EM. [Laws Governing the Separation of Elements Accompanying Copper in the Reverberatory Furnace.] *Metall u. Erz.*, vol. 30, 1933, pp. 340-343; *Chem. Abs.*, vol. 27, 1933, p. 5283.

Laws governing the reaction dynamics of O and their influence upon the quantitative separation of Pb , Co , Ni , Fe , Sb , and P are considered. Most favorable conditions for separating the individual elements are established.

702. MILLIGAN, W. O., AND MERTON, L. X-ray Diffraction Studies in the System Nickel Oxide-Aluminum Oxide. *Jour. Phys. Chem.*, vol. 50, 1946, pp. 465-470; *British Abs.*, 1947, p. A-I-148.

In the air-dried gels of $\text{NiO-Al}_2\text{O}_3$ obtained by precipitation from mixtures of $\text{Ni}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ (anhydrous NiO content, 0 to 100 molecular percent) each oxide protects the other against crystallization at room temperature and the protective action remains marked at 500° , 700° , and $1,000^{\circ}\text{C}.$

703. PASSERINI, L. [Solid Solutions, Isomorphism, and Symmorphisms Among Oxides of Bivalent Metals. II. The Systems CoO-NiO , CoO-MgO , CoO-CdO , NiO-MgO , NiO-MnO , and NiO-CdO .] *Gazz. chim. ital.*, vol. 59, pp. 144-154; *Chem. Abs.*, vol. 23, 1929, p. 4125².

All possible binary systems were studied among ZnO , MgO , NiO , CoO , MnO , CdO , CaO , SrO , and BaO , but in the present paper only the systems above are described in detail. In the systems CoO-NiO , CoO-MgO , CoO-MnO , and NiO-MgO , miscibility between the oxides is complete, and the displacement of the lattice is proportional to the percent composition. In the system NiO-MnO the solubility of the oxides was, under the conditions, only partial.

704. ROTH, W. A., AND HAVEKOS, H. [The Heat of Formation of Cobaltous Oxide.] *Ztschr. anorg. allgem. Chem.*, vol. 195, 1931, pp. 239-240; *Chem. Abs.*, vol. 25, 1931, p. 3233².

Outgassed, Ni -free Co containing 3.6 percent CoO was burned in a calorimetric bomb. After correction for Co_2O_3 and unburned Co , the heat of formation of CoO was 57.2 ± 0.2 kg.-cal.

705. SALMANG, H. [The Pyrochemical Series of Oxides.] *Ztschr. angew. Chem.*, vol. 44, 1931, pp. 908-912; *Chem. Abs.*, vol. 26, 1932, p. 2387.

By studying the corrosion of fireproof material under the influence of silicate fusions, it was found that metallic oxides could be arranged according to their reactivity in a tension series, which is called the pyrochemical series. In this series, oxides of the type R_2O and RO are basic, while those with more O are acid. The alkalis are an apparent exception because they are only slightly dissociated.

706. SCHENCK, RUDOLPH, AND WESSELKOCK, H. [The Activation of Metals by Addition of Foreign Substances.] *Ztschr. anorg. allgem. Chem.*, vol. 184, 1929, pp. 39-57; *Chem. Abs.*, vol. 24, 1930, p. 2035².

The effect of CaO , MgO , MnO , and Al_2O_3 separately and Al_2O_3 and MgO jointly on the oxidation of Ni and Co at 900°C . in an atmosphere of CO was studied.

707. SHIBATA, Z., AND MORI, I. [Reduction Equilibrium Between Metallic Oxide and Hydrogen. I. Measurement of $\text{CoO} + \text{H}_2 \rightleftharpoons \text{Co} + \text{H}_2\text{O}$ by New Methods.] *Ztschr. anorg. allgem. Chem.*, vol. 212, 1933, pp. 305-316 (see *Chem. Abs.*, vol. 27, 1933, p. 1807); *Chem. Abs.*, vol. 27, 1933, p. 4468.

The equilibrium $\text{CoO} + \text{H}_2 \rightleftharpoons \text{Co} + \text{H}_2\text{O}$ was studied at 921° , 821° , 721° , 622° , 522° , and 422°C . The relation between the equilibrium constant K and temperature is: $\log K = (494.191/T) + 1.08690$. The dissociation pressure of CoO and the equilibrium of H_2O gas at 400° - $1,000^\circ\text{C}$. are calculated.

708. SIEBE, P., AND BUSSE, C. [Course of Oxidation of Fluid Copper Melts With Small Quantities of Nickel, Arsenic, Tin, and Antimony.] *Metall u. Erz.*, vol. 30, 1933, pp. 273-280; *Chem. Abs.*, vol. 27, 1933, p. 5283.

The course of oxidation of Sn , Ni , As , and Sb was followed by chemical analysis, photomicrography and electric conductivity measurements.

709. SKAPSKI, ADAM, AND DABROWSKI, JOSEPH. [The Equilibrium and Heat of Reaction of the Reaction $\text{NiO} + \text{H}_2 = \text{Ni} + \text{H}_2\text{O}$.] *Ztschr. Electrochem.*, vol. 38, 1932, pp. 365-370; *Chem. Abs.*, vol. 26, 1932, p. 4527.

710. TEVOSOV, S. P. [Forms of Adsorption of Oxygen, Carbon Monoxide, and Carbon Dioxide on Nickel Oxide.] *Trudy Inst. Khim. Akad. Nauk. Azerbaidzhan, S. S. S. R.*, vol. 13, 1954, pp. 29-36 (in Russian); *Chem. Abs.*, vol. 49, 1955, p. 9350h.

From 80° to 100°C . the adsorption of O_2 on Ni oxide is of molecular type. Carbon monoxide at temperatures under 0°C . also shows molecular adsorption, but above 0°C . the activated type of adsorption takes place. Carbon dioxide adsorption from -19.5° to 100°C . is of the activated type. The adsorption characteristics of the oxide depend on the type of preparation and on its magnetic susceptibility. The highest susceptibility occurs in the oxide prepared by hydrolysis of the NH_3 complex, whereas a specimen prepared by heating the nitrate to 500°C . has a very low magnetic susceptibility; the same order of activity is found in the adsorption by these specimens. The oxide prepared from the complex has the composition $\text{NiO}_{1.2}-0.5\text{H}_2\text{O}$.

711. TSEIDLER, A. A., AND ZAREMBA, N. I. [Interaction of Cupric Oxide and Nickelous Oxide as Affected by Temperature and Duration of Roasting.] *Tsvetnye Metal.*, vol. 20, No. 2, 1947, pp. 42-43; *Chem. Abs.*, vol. 42, 1948, p. 4103a.

A 6 : 1 mixture of NiO and CuO was roasted at 300° - 900°C . for various lengths of time to determine the effect of temperature and time on the solubility of Cu in the leaching (10 percent H_2SO_4) process as practiced in the Hybinette process and to test the contention that, in the course of the roasting, NiO and CuO react to form a compound insoluble in the leaching solution. Roasting at temperatures below 600°C . did not affect the solubility of Cu . Above 600°C . the components combined in some form that reduced the solubility of Cu greatly. The compound formed above 600°C . is suggested to be $3\text{NiO} \cdot \text{CuO}$. The extent to which the oxides combined to form the insoluble product increased with duration of roasting.

712. WARTENBERG, H. V., AND PROPHET, E. [Melting-Point Diagrams of Highly Refractory Oxides. V. Systems With Magnesia.] *Ztschr. anorg. allgem. Chem.*, vol. 208, 1932, pp. 369-379 (see *Chem. Abs.*, vol. 26, 1932, p. 5239); *Chem. Abs.*, vol. 27, 1933, p. 656.

713. WATANABE, MOTOO. The Equilibrium in the Re-

duction of Nickelous Oxide by Carbon Monoxide. *Bull. Inst. Phys. Chem. Research*, vol. 9, No. 6, 1930, pp. 477-483 (pub. with *Sci. Papers Inst. Phys. Chem. Research*, Tokyo, vol. 13, 1930, pp. 246-253); *Chem. Abs.*, vol. 24, 1930, p. 5582⁶.

The equilibrium in the reduction of NiO by CO was studied between 663° and 852°C . The relation between the dissociation constant and the temperature is given by $\log K_p = (2590/T) - 0.1082$. Entropy of NiO at 25°C . is calculated as 8.97 calories per degree. The dissociation pressure of NiO at 25°C . $= 1.2 \times 10^{-7}$ mm. Hg.

714. ———. The Equilibrium in the Reduction of Cobaltous Oxide by Carbon Monoxide. *Bull. Inst. Phys. Chem. Research*, Tokyo, vol. 9, pp. 676-682 (abs. 62-63 (in English), pub. with *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), vol. 14, Nos. 262-263, 1930); *Chem. Abs.*, vol. 25, 1931, p. 3225¹.

715. ———. The Dissociation Pressure of Cobalt-Cobaltic Oxide. *Bull. Inst. Phys. Chem. Research*, Tokyo, vol. 12, 1933, pp. 255-261 (abs. in English, pub. with *Sci. Papers Inst. Phys. Chem. Research*, Tokyo, vol. 20, pp. 404-408); *Chem. Abs.*, vol. 27, 1933, p. 2617.

716. ———. [Equilibrium in the Reduction of Cobaltous Oxide by Carbon Monoxide.] *Sci. Repts. Tôhoku Imp. Univ.*, 1st ser., vol. 22, 1933, pp. 892-901; *Chem. Abs.*, vol. 28, 1934, p. 1914⁶.

The equilibrium of the reduction of CoO by CO was studied by a dynamic method from 563° - 861°C . Thermodynamic values for CoO were calculated from experimental results and other data.

717. ———. [Equilibrium in the Reduction of Nickelous Oxide by Carbon Monoxide.] *Sci. Repts. Tôhoku Imp. Univ.*, 1st ser., vol. 22, 1933, pp. 436-447; *Chem. Abs.*, vol. 28, 1934, p. 2249⁴.

718. WÖHLER, L., SHIBATA, ZEN-ICHI, AND KUNST, R. [Reduction Equilibrium of Metallic Oxides. IV. A New Precise Method of Determination of the Reduction Equilibrium Between Metallic Oxide and Hydrogen.] *Jour. Chem. Soc., Japan*, vol. 54, 1933, pp. 44-49; *Chem. Abs.*, vol. 27, 1933, p. 1807.

Describes a modification of Deville's method of studying the reduction of metallic oxide, together with an improved method of measuring the partial pressure of H_2 . The error in the measurement is reduced to one-tenth of that of Deville's method.

719. ZUR STRASSEN, H. [Equilibrium Among Iron, Nickel, and Their Silicates in a State of Fusion.] *Ztschr. anorg. allgem. Chem.*, vol. 191, 1930, pp. 209-245; *Chem. Abs.*, vol. 24, 1930, p. 5581⁸.

In the reaction $\text{Fe} + \text{NiSiO}_3 \rightleftharpoons \text{Ni} + \text{FeSiO}_3$, equilibrium can be obtained without shaking or stirring and follows the ideal mass-action law. It is independent of the composition of the silicate phase as well as the presence of impurities.

NONOXIDES

720. ALLWÖRDEN, H. V., AND KOHLMAYER, E. J. [The Decomposition of Metal Sulfides by Carbon at High Temperatures.] *Metall u. Erz.*, vol. 36, 1939, pp. 578-584; *Chem. Abs.*, vol. 35, 1941, p. 7909⁷.

Several hundred grams of metal sulfide was melted in a cylindrical C crucible and heated at various temperatures and for various times. Cobalt sulfide, NiS , and other metallic sulfides were studied. Above certain temperatures characteristic boiling phenomena, accompanied by rapid expulsion of gas, took place.

721. BILTZ, W., VOIGT, A., MEISEL, K., WEIBKE, F., AND EHRLICH, P. [Affinity LXIX. System Nickel Monosulfide, Nickel Disulfide-Sulfur.] *Ztschr. anorg. Chem.*, 1936, pp. 275-296; (see *British Chem. Abs.*, 1935, p. 1335); *British Chem. Abs.*, 1936, p. A-1204.

Tensimetric data show that no compound exists between NiS and NiS₂. The transformation temperature of NiS from trigonal to hexagonal is 396° C.

722. BORCHERS, HEINZ, AND HERMANN, GERHARD. [Oxidation of Metal Sulfides by Roasting.] *Bol. minero. soc. nacl. minero* (Santiago, Chile), No. 583, 1948, pp. 650-657; *Chem. Abs.*, vol. 48, 1954, p. 516d.

Sulfo salts (one sample with the composition As 37.9, Fe 19.1, Co 18.6, Ni 17.8, and S 5.9), were roasted at temperatures between 600° and 1,000° C. Eight graphs showing changes in composition with variations in temperature and time of roasting are given. Changes in density of 12 samples before and after roasting are tabulated.

723. GERASIMOV, J. I., PIRTZHALOV, N. I., AND STEPIN, V. V. [Thermal Dissociation of Higher Sulfides of Nickel.] *Jour. Ind. Chem.*, Russia, vol. 13, 1936, pp. 1273-1283; *British Chem. Abs.*, 1937, p. A-I-130.

The preparation of NiS₂ from NiS and S is possible at 500° C. The vapor pressure at 700°-750° C. of the sulfides represented by NiS_{1-x} rises abruptly when the S content is greater than that of NiS_{1-x} (NiS₂?). Formation of the solid solutions NiS₂-NiS_{1-x} and NiS_{1-x}-NiS₂ is suggested by the analytical and vapor-pressure data.

724. HAUFFE, K., AND RAHMEI, A. [Mechanism of Sulfiding of Iron, Nickel, and Nickel Alloys at High Temperatures.] *Ztschr. physikal. Chem.*, vol. 199, 1952, pp. 152-169; *British Abs.*, 1952, p. B-I-1377.

The reaction of Fe with S vapor at 670° C. and S vapor pressure (*p*) 0.1-100 mm. to give FeS was followed gravimetrically in a static apparatus. The rate of reaction of Ni and Ni-Ag (0.1-1 percent atomic percent of Ag) and Ni-Cr alloys (0.1-1 percent of Cr) with S vapor was followed at 630° C. and a vapor pressure of 10⁻³ to 1 mm. The reaction occurs mainly by diffusion of S through the porous surface film.

725. HÜLSMANN, O., MEISEL, K., AND BILTZ, W. [Affinity LXV. Tensimetric Analysis of System CoS-CoS₂.] *Ztschr. anorg. Chem.*, vol. 224, 1935, pp. 73-83; *British Chem. Abs.*, 1935, p. A-1335.

The highest sulfide of Co is CoS₂, which is partly miscible with both S and CoS. The reported CoS₂, from the action of H₂S on complex Co salts, is a mixture of CoS and CoS₂. Linneite, Co₃S₄, is not formed during the tensimetric degradation of CoS₂.

726. HÜLSMANN, H., WEIBKE, F., AND MEISEL, K. [Lower Cobalt Sulfides, Equilibrium Diagram of System Co-CoS₂.] *Ztschr. anorg. Chem.*, vol. 227, 1936, pp. 113-123 (*see* *British Chem. Abs.*, 1935, p. A-1335); *British Chem. Abs.*, 1936, p. A-797.

727. JANDER, W., AND KRIEGER, A. [Equilibria Between Metals, Sulfides, and Silicates in the Melt. V. Equilibria Fe+CoO=Co+FeO and Ni+CoO=Co+NiO in the Melt.] *Ztschr. anorg. Chem.*, vol. 232, 1937, pp. 39-56 (*see* *British Chem. Abs.*, 1934, pp. A-365 and A-734); *British Chem. Abs.*, 1937, p. A-308.

728. JANDER, W., ZWEYER, H., AND SENF, H. [Equilibria Between Metals, Sulfides, and Silicates in the Fused Condition. IV. The Heterogeneous Equilibrium FeS+Ni Silicate=NiS+Fe Silicate in the Fused Condition.] *Ztschr. anorg. allgem. Chem.*, vol. 217, 1934, pp. 417-426 (*see* *Chem. Abs.*, vol. 28, 1934, p. 3290⁶); *Chem. Abs.*, vol. 28, 1934, p. 4328⁶; *British Chem. Abs.*, 1934, p. A-734.

729. KELLEY, K. K. Contributions to the Data on Theoretical Metallurgy. I. The Entropies of Inorganic Substances. Bureau of Mines Bull. 350, 1932, Cobalt, p. 23.

730. ———. Contributions to the Data on Theoretical Metallurgy. I. The Entropies of Inorganic Sub-

stances. Bureau of Mines Bull. 350, 1932, Specific Heat and Entropy of Nickel Metal, p. 34.

731. ———. Contributions to the Data on Theoretical Metallurgy. III. The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances. Bureau of Mines Bull. 383, 1935, Cobalt, p. 43, and Nickel, pp. 72-74.

732. ———. Contributions to the Data on Theoretical Metallurgy. VI. A Revision of the Entropies of Inorganic Substances. Bureau of Mines Bull. 394, 1935, Nickel, p. 21.

733. ———. Contributions to the Data on Theoretical Metallurgy. VII. The Thermodynamic Properties of Sulfur and Its Inorganic Compounds. Bureau of Mines Bull. 406, 1937, Nickel Sulfate, p. 103.

734. ———. Contributions to the Data on Theoretical Metallurgy. VII. The Thermodynamic Properties of Sulfur and Its Inorganic Compounds. Bureau of Mines Bull. 406, 1937, Cobalt Sulfide, p. 34.

735. ———. Contributions to the Data on Theoretical Metallurgy. IX. The Entropies of Inorganic Substances (rev.). Bureau of Mines Bull. 434, 1941, Cobalt Metal and Cobalt Chloride, p. 9.

736. ———. Contributions to the Data on Theoretical Metallurgy. IX. The Entropies of Inorganic Substances (rev.). Bureau of Mines Bull. 434, 1941, Nickel, Nickel Oxide, Nickel Chloride, and Nickel Carbonate, p. 57.

737. KLEINHEISTERKAMP, HERMAN. [Fundamental Equilibria in the Formation of Metallurgical Speisses.] *Erzbergbau u. Metallhüttenw.*, vol. 1, 1948, pp. 65-72; *Chem. Abs.*, vol. 43, 1949, p. 1696c.

The great number of substances participating in speiss formation makes exact observation and description of the action of individual components difficult. The phases of the melt known as speisses and alloys are identified. Phase diagrams of speisses and alloys of systems not previously investigated include As and S with Cu, Fe, Ni, or Pb combinations. A useful application of this knowledge is the control of speiss formation and the decoppering of a speiss in the most advantageous manner.

738. MAIER, C. G. Vapor Pressures of the Common Metallic Chlorides and a Static Method for High Temperatures. Bureau of Mines Tech. Paper 360, 1925, Nickel Chloride, pp. 31-32; and Cobalt Chloride, pp. 33-34.

739. RESNIK, I. D. [Calculation of the Optimum Composition of the First Matte.] *Tsvetnye Metal*, vol. 19, No. 4, 1946, pp. 41-44; *Chem. Abs.*, vol. 41, 1947, p. 1967d.

Equations are derived for calculating the optimum composition of the first matte in smelting Ni. Generally, poor first mattes insure better extraction. The decision on poor vs. rich first mattes must take into account the cost of recovering Ni from the converter slag when the slag is processed for some other metal, the possibility of using poor first matte in the existing installation, and other technological circumstances.

740. ROSENQVIST, TERKEL (University of Chicago). A Thermodynamic Study of Iron, Cobalt, and Nickel Sulfides. *Jour. Iron and Steel Inst.*, London, vol. 176, 1954, pp. 37-57; *Chem. Abs.*, vol. 48, 1954, p. 11,127a.

741. SANO, KOKICHI [The Equilibrium in the Reduction of Cobalt Chloride With Hydrogen.] *Jour. Chem. Soc., Japan*, vol. 58, 1937, pp. 370-375 (*see* Shibata and Kitagawa, *Chem. Abs.*, vol. 29, 1935, p. 7161); *Chem. Abs.*, vol. 31, 1937, p. 5248⁶.

742. ———. [The Thermodynamic Values of Nickelous Chloride.] *Jour. Chem. Soc., Japan*, vol. 58,

- 1937, pp. 376-378 (*see* preceding abs.); Chem. Abs., vol. 31, 1937, p. 5248^o.
743. SANO, KOKICHI (Nagoya University). [The Reduction Equilibria of Cobaltous Chloride and Nickelous Chloride by Hydrogen.] F. Ishikawa Anniversary vol., Sci. Repts., Tôhoku Univ., vol. 37, No. 1, 1953, pp. 1-8; Chem. Abs., vol. 48, 1954, p. 6793b.
744. SCHENCK, RUDOLF, AND DER FORST, PETER. [Equilibrium Studies of Ore-Forming Sulfides II.] Ztschr. anorg. allgem. Chem., vol. 241, 1939, pp. 145-157 (*see* Chem. Abs., vol. 33, 1939, p. 2858^o); Chem. Abs., vol. 33, 1939, p. 6761^o.
- The authors report on equilibrium ratios between various Ni sulfides, reversibility or irreversibility of formation of sulfides, and equilibria of phases in systems that may contain Ni, S, Sb, and Bi.
745. SCHENCK, RUDOLF, AND RAUB, ERNST (University of Münster, in W.). [Equilibrium Studies in the Systems Cobalt-Sulfur-Oxygen and Nickel-Sulfur-Oxygen.] Ztschr. anorg. allgem. Chem., vol. 178, 1929, pp. 225-251 (*see* Chem. Abs., vol. 21, 1927, p. 3865); Chem. Abs., vol. 23, 1929, p. 2641^o.
746. SHAKHOV, G. A., AND KRUGLOVA, A. A. [Mineralogical Study of Bessemer Matte.] Tsvetnye Metal, vol. 20, No. 2, 1947, pp. 40-41; Chem. Abs., vol. 42, 1948, p. 4106b.
- A Bessemer matte was studied using a microscope, a print on gelatin paper, and chemical analysis. Sulfides and metallic Ni particles were identified. It is indicated that the basic mass of sulfides is in the form Ni_3S_2 and not NiS , as suggested by Guertler (Chem. Abs., vol. 26, 1932, p. 2947^o).
747. SIEGEL, SIDNEY, AND SHULL, C. G. Superlattice Presence in Cu_3Au and FeCo Systems. Tech. In. Branch AEC, Oak Ridge, Tenn., Apr. 6, 1949, AECD 2077. U. S. Government Publications, Monthly Catalog, 1949, Supt. Documents, item 10927.
748. SUDO, KINGO. [Fundamental Researches on the Smelting of Sulfide Ores. V. The Equilibrium in the Reduction of Solid Cobaltous Sulfide by Hydrogen Gas.] Sci. Repts. Research Inst. Tôhoku Univ., ser. A, 1950, pp. 507-512 (*see* Chem. Abs., vol. 45, 1951, p. 10,011f); Chem. Abs., vol. 46, 1952, p. 4347h.
749. ——— (Tôhoku University, Sendai). [Smelting of Sulfide Ores. XI. Equilibria in the Reduction of Solid Nickel Sulfides by Hydrogen Gas.] Sci. Repts. Research Inst., Tôhoku Univ., ser. A, vol. 4, 1952, pp. 182-190 (in English) (*see* Chem. Abs., vol. 47, 1953, p. 3067d, preceding abs.); Chem. Abs., vol. 47, 1953, p. 6321i.
750. TSEIDLER, A. A. [The Influence of the Reducibility of the Iron in the Ore on the Nickel Content of the First Matte.] Tsvetnye Met., vol. 16, No. 20, 1941, pp. 24-28; Chem. Zentralbl., vol. II, 1944, pp. 1111-1112; Chem. Abs., vol. 41, 1947, p. 6500a.
- The Ni content of the first matte is influenced not only by the amount of nonreducible iron but also by the Ni content of the ore. To compensate for the influence of the varying Ni content of the samples a coefficient N is calculated according to the following formula: $N = (\text{percent Fe in the ore}) \times (\text{percent reducible Fe}) / [(\text{percent Ni in the ore}) \times (100)]$. The Ni content of the first matte decreases linearly with increasing value of N . It is most advantageous to fuse ores that contain large enough amounts of Fe in difficultly reducible form. In this way a first matte of acceptable composition is obtained, and the slag contains enough iron oxide to render it easily fusible.
751. VOGEL, RUDOLF, AND TONN, WILLI. [The Ternary System: Iron-Nickel-Sulfur.] Arch. Eisenhüttenw., vol. 3, 1930, pp. 769-780; Chem. Abs., vol. 25, 1931, p. 672.

The equilibria in the field $\text{Fe-FeS-Ni}_3\text{S}_2\text{-Ni}$ of the system Fe-Ni-S are investigated, thermal, microscopic, and magnetic methods being used. In this field, four primary saturation surfaces are determined on cooling the melt, the primary separation therefrom being: Δ - Fe-Ni mixed crystals (M), γ - Fe-Ni M FeS , and the S-rich M .

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752. BAWN, C. E. H. The Kinetics of the Decomposition of Nickel Carbonyl. Trans. Faraday Soc., vol. 31, 1935, pp. 440-446; Chem. Abs., vol. 29, 1935, p. 2826^o.
- The decomposition of Ni(CO)_4 in Ni-coated vessels, $\text{Ni(CO)}_4 \rightleftharpoons \text{Ni} + 4\text{CO}$ was investigated in the temperature range $100^\circ\text{--}128^\circ\text{C}$. The reactions were 80 percent homogeneous and 20 percent heterogeneous, both reactions being inhibited by CO, and having the same relationship: $dx/dt = k_{\text{Ni(CO)}_4} / (1 - k'_{\text{CO}})$. Equations showing the decomposition of Ni(CO)_4 in more than one step are given, which yield this rate law. A preliminary study of the oxidation of Ni(CO)_4 , indicated definite explosion limits.
753. BEHRENS, HELMUT, AND LOHÖFER, FREIMUTH (Technical Institute, Munich, Germany). [Nickel Carbonyl Hydride, $[\text{NiH(CO)}_3]_2$, a New Type of Carbonyl Hydride.] Ztschr. Naturforsch., vol. 8b, 1953, pp. 691-692 (*see* Chem. Abs., vol. 46, 1952, p. 8562a); Chem. Abs., vol. 48, 1954, p. 5012f.
- Nickel carbonyl reacts with a Na solution in liquid ammonia according to $2\text{Ni(CO)}_4 + 2\text{Na} + 2\text{NH}_3 \rightarrow [\text{NiH(CO)}_3]_2 + 2\text{CO} + 2\text{NaNH}_2$. More than the stoichiometrical amount of Na is used and less CO formed, owing to NaCO formation. Since both NaNH_2 and NaCO are difficultly soluble in NH_3 , a pure solution of $[\text{NiH(CO)}_3]_2$ is obtained. Here the H is not acidic and cannot be replaced by a metal. On evaporation of the NH_3 the red $[\text{NiH(CO)}_3]_2 \cdot 4\text{NH}_3$ is obtained. A molecular weight determination shows dimer structure. The reaction with acid demonstrates that Ni is in the -1 oxidation state: $2[\text{NiH(CO)}_3]_2 + 2\text{H}^+ \rightarrow 3\text{Ni(CO)}_4 + \text{Ni}^{2+} + 3\text{H}_2$.
754. BLANCHARD, A. A., AND GILMONT, PAUL. Preparation of Cobalt Carbonyl, Cobalt Nitrosyl Carbonyl, and Cobalt Carbonyl Hydride by the Cyanide Method. Jour. Am. Chem. Soc., vol. 62, 1940, pp. 1192-1193; Chem. Abs., vol. 34, 1940, p. 4354^o.
- An alkaline suspension of a cobalt salt absorbs CO almost quantitatively to form KCo(CO)_4 , but only in the presence of a carrier such as a small amount of a cyanide. Treatment of KCo(CO)_4 with NO gives Co(NO)(CO)_3 . Addition of an excess of HCl to the reaction mixture gives the volatile HCo(CO)_4 , which condenses at -79°C . to a solid; it melts at -33°C . and decomposes above that temperature into $[\text{Co(CO)}_4]_2$ and H.
755. BLANCHARD, A. A., AND WINDSOR, M. M. The Significance of the Hydrides of the Carbonyls of Iron and Cobalt. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 826-827; Chem. Abs., vol. 28, 1934, p. 3018^o.
- The electronic structure proposed for Ni(CO)_4 (Chem. Abs., vol. 20, 1926, p. 1570); also exists in $\text{Fe(CO)}_5\text{H}_2$ (Chem. Abs., vol. 26, 1932, pp. 935 and 3198) and $\text{Co(CO)}_4\text{H}$ (Chem. Abs., vol. 28, 1934, 106^o), where H furnishes the extra electrons necessary to complete the Ni(CO)_4 pattern. In nitrosyl carbonyls and polymeric carbonyls the same electron pattern is completed.
756. BLANCHARD, A. A., RAFTER, J. R., AND ADAMS, W. B. JR. Formation of Carbonyls and Related Compounds. Jour. Am. Chem. Soc., vol. 56, 1934, pp. 16-17 (*see* Chem. Abs., vol. 27, 1933, p. 3416); Chem. Abs., vol. 28, 1934, p. 983^o.

Carbonyls of Ni and Co and cobalt nitrosyl tri-carbonyl were prepared by treating alkaline suspensions of sulfide or cyanide with CO or CO-NO mixture. Gives vapor-pressure and vapor-density data for $\text{CoNO}(\text{CO})_3$.

757. BROCKWAY, L. O., AND CROSS, P. C. The Molecular Structure of Nickel Carbonyl. *Jour. Chem. Physics.*, vol. 3, 1935, pp. 828-833; *Chem. Abs.*, vol. 30, 1936, p. 663².

Electron diffraction by the vapor of $\text{Ni}(\text{CO})_4$ indicates a molecular model in which the CO groups have a tetrahedral arrangement about the Ni atom with the distances $\text{Ni}-\text{C}=1.82\pm0.03$ Å, and $\text{C}-\text{O}=1.15$ Å. These distances are compatible with resonance between two electron structures in which the C-O bond resonates between triple and double electron pair bonds, and the Ni-C bond between single and double electron pair bonds. Nickel carbonyl is the first quadrivalent compound of neutral Ni whose structure has been determined, and its tetrahedral configuration is contrasted with the square arrangement of bonds in the quadrivalent compounds of Ni.

758. COLEMAN, G. W., AND BLANCHARD, A. A. Preparation and Properties of Cobalt Nitrosyl Carbonyl and of Cobalt Carbonyl Hydride. *Jour. Am. Chem. Soc.*, vol. 58, 1936, pp. 2160-2163 (*see Chem. Abs.*, vol. 28, 1934, p. 3018³); *Chem. Abs.*, vol. 31, 1937, p. 333⁴.

The method of Schubert (*Chem. Abs.*, vol. 28, 1934, p. 106⁵) for making $\text{CoNO}(\text{CO})_3$ has been improved. Absorption of CO by alkaline Co salt solutions is not only promoted by cysteine but to a lesser extent by tartrate, other organic $-\text{OH}$ and $-\text{NH}_2$ acids, KCN and sulfides. Bromine displaces NO and CO quantitatively from $\text{CoNO}(\text{CO})_3$. Acidifying $\text{KCo}(\text{CO})_3$ liberates $\text{HCo}(\text{CO})_3$. This is very volatile and condenses to light-yellow crystals, melting at -33°C . to a sulfur-yellow liquid. At room temperature it decomposes to $\text{Co}_2(\text{CO})_8$ and H_2 . The acid $\text{HCo}(\text{CO})_3$ is stronger than H_2CO_3 .

759. ERCOLI, ROFFAELE, AND BARBIERI-HERMITTE, FRANCO (Politec. Milan). [The Equilibrium Between $[\text{Co}(\text{CO})_4]_2$ and $[\text{Co}(\text{CO})_3]_2$.] *Atti accad. nazl. Lincei Rend. Classe sci. fis. mat. e nat.*, vol. 16, 1954, pp. 249-257; *Chem. Abs.*, vol. 48, 1954, p. 10,408i.

The pressure variations with time and the equilibrium pressures at different concentrations of $[\text{Co}(\text{CO})_4]_2$ in the reaction $2[\text{Co}(\text{CO})_4]_2 \rightleftharpoons [\text{Co}(\text{CO})_3]_2 + 4\text{CO}$ were determined in an autoclave. The results are shown in three figures. At temperatures above 120°C . a solid phase of the tricarbonyl is probably formed. The equilibrium constants between 73° and 137°C . are given in a table. The average heat of reaction was 33,000 cal.

760. GILLILAND, W. L., AND BLANCHARD, A. A. Nickel Tetra-Carbonyl. *Inorg. Syntheses II*, 1946, 294 pp., pp. 234-237 (*see Mond, Robert, Jour. Soc. Chem. Ind.*, vol. 14, 1895, p. 945); *Chem. Abs.*, vol. 40, 1946, p. 7030⁶.

761. HIEBER, WALTER. [Hydrogen Metal Carbonyls: Formation of Hydrogen Cobalt Carbonyl, $\text{Co}(\text{CO})_4\text{H}$.] *Ztschr. Elektrochem.*, vol. 40, 1934, pp. 158-159; *Chem. Abs.*, vol. 28, 1934, p. 3328¹.

Cobalt tetracarbonyl in alkaline solution forms $\text{Co}(\text{CO})_4\text{H}$, which decomposes readily. Replacement of the H by a complex cation (for example $\text{Ni}(\text{NH}_3)_6^{+}$), stabilizes the molecule. Differences between this new class of compounds and hydrides are indicated. Carbonyls of the Cr group metals and Ni do not form H carbonyls, possibly because the number of CO groups equals the coordination number of the metal.

762. ———. [The Present Status of the Chemistry of the Metal Carbonyls.] *Die Chemie*, vol. 55, 1942,

pp. 7-11 (*see Chem. Abs.*, vol. 36, 1942, p. 1256⁹); *Chem. Abs.*, vol. 37, 1943, p. 2293¹.

Reviews history of metal carbonyls, their direct synthesis, and recent methods of production are reviewed. The present high-pressure synthesis of metal carbonyls is described in general and specifically for the formation of $[\text{Co}(\text{CO})_4]_2$ from Co compounds and for heavy metal derivatives of cobalt carbonyl hydrate. (*See work cited above*, pp. 24-28.) A system of the metal carbonyls, based on the periodic system of the elements, is developed in which monomeric and polymeric compounds are given for each period, inclusive of the carbonyls of maximum CO content, which often has a constitution with complete shell configuration. In each period the stability of the carbonyls, starting from the hexacarbonyls, decreases toward the right.

763. HIEBER, W., AND FACK, E. [Metal Carbonyls. XXVII. Heavy Metal Derivatives of Metal Carbonyl Hydrides.] *Ztschr. anorg. allgem. Chem.*, vol. 236, 1938, pp. 83-106; *Chem. Abs.*, vol. 32, 1938, p. 3715⁵.

A salt structure can be ascribed only to those compounds that have coordinately saturated complex cations such as the hexamines or the tri-o-phenanthroline group. The central metal atom of the amine cation has given 1 electron to each of the radicals $[\text{HFe}(\text{CO})_4]$ and $[\text{Co}(\text{CO})_4]$. The anions $[\text{HFe}(\text{CO})_4]$ and $[\text{Co}(\text{CO})_4]^-$ have a symmetrical electron arrangement. They are unstable by themselves but are stabilized by the salt formation with strong complex cations. Compounds of the Cu and Zn group are mixed metal carbonyls and not of the salt type. Describes preparation of several metal compounds and complexes.

764. HIEBER, W., AND FISCHER, E. O. (Technische Hochschule, Munich, Germany). [Metal Carbonyls. LII. The Reaction of Carbon Monoxide With Ni(II) and Co(II) in the Presence of Sodium Dithionate.] *Ztschr. anorg. allgem. Chem.*, vol. 269, 1952, pp. 292-307; *Chem. Abs.*, vol. 47, 1953, p. 3169e.

Nickel and cobalt salts in ammoniacal solution and in the presence of sodium dithionate are almost quantitatively converted to their respective carbonyls by CO.

765. HIEBER, W., AND HÜBEL, W. (Technische Hochschule, Munich, Germany). [Metal Carbonyls. LX. The Acid Function of the Carbonyl Hydrides of Cobalt and Iron.] *Ztschr. Elektrochem.*, vol. 57, 1953, pp. 235-243 (*see Chem. Abs.*, vol. 44, 1950, p. 9851b; vol. 46, 1952, p. 8562b; and vol. 47, 1953, pp. 3169f, 11,063f, and 12,090i); *Chem. Abs.*, vol. 48, 1954, p. 71g.

Potentiometric titration (glass electrode) of $\text{HCo}(\text{CO})_3$ in aqueous solution showed complete dissociation into $\text{Co}(\text{CO})_3^-$ and H^+ . In CH_3OH and glacial AcOH instead of H_2O , in which it is only slightly soluble, $\text{HCo}(\text{CO})_3$ has an acid strength comparable to that of HNO_3 . Potentiometric titration of $\text{Ba}[\text{Fe}(\text{CO})_4]$ showed that $\text{H}_2\text{Fe}(\text{CO})_4$ is a weak dibasic acid with dissociation constants $K_1=3.6\times10^{-5}$ and $K_2=10^{-11}$.

766. HIEBER, WALTER, AND KAUFMANN, HANS. [XIV. The Chemical Properties of Nickel Carbonyl Compared With Those of Iron Carbonyl.] *Ztschr. anorg. allgem. Chem.*, vol. 204, 1932, pp. 174-183; *Chem. Abs.*, vol. 26, 1932, p. 1868.

Basic substances, such as NaOMe , aqueous KOH , and $(\text{NH}_3)_2$, do not react with nickel carbonyl, although the alkaline solutions are extremely sensitive to O_2 . In general, the Ni compound is much less reactive than the Fe compounds, either remaining unchanged or breaking down completely to CO and Ni salts.

767. HIEBER, WALTER, AND SCHULTEN, H. [Formation and Reactions With Metal Salts of Cobalt Carbonyl Hydride.] *Ztschr. anorg. allgem. Chem.*, vol. 232,

- 1937, pp. 17-28 (*see* Chem. Abs., vol. 29, 1935, p. 2468¹); Chem. Abs., vol. 31, 1937, p. 4917¹.
- Solutions of $\text{HCo}(\text{CO})$, prepared by agitating 1-1.5 gm. of $\text{Co}(\text{CO})$, in vacuo with 100-175 cc. of concentrated aqueous NH_3 for 36 hr. were used for reactions with metal salts. Directions are given for forming salts with mercury, silver, and nickel, and their properties are described. To prepare cobalt carbonyl hydride (pp. 29-38), the cobalt carbonyl is reacted for 36 hr. with $\text{Ba}(\text{OH})_2$. This was added under reduced pressure to HPO_4 and distilled through several cold traps.
768. HIEBER, WALTER, AND SCHULTEN, H. [XXIX. The Mechanism of the High-Pressure Synthesis of Cobalt Carbonyl From Cobalt Halides.] *Ztschr. anorg. allgem. Chem.*, vol. 243, 1939, pp. 145-163 (*see* Chem. Abs., vol. 33, 1939, p. 3285²); Chem. Abs., vol. 34, 1940, p. 5367².
- When the cobalt halides were heated for 15 hr. with CO under a pressure of 200 atmospheres in a container lined with Ag or Cu, the halogen was precipitated as AgX or CuX , and $\text{Co}(\text{CO})_4$ was produced. The chloride gave a yield of 4.5 percent at 300° C., the bromide gave 4.5 percent at 200° C., but the iodide gave 100 percent at 150° C. Small amounts of cuprous carbonyl halides, $\text{CuBr} \cdot \text{CO}$ and $\text{CuI} \cdot \text{CO}$ are produced in the reactions; similarly, cobalt carbonyl iodides, $\text{CoI}_2 \cdot \text{CO}$, is produced and by its easy decomposition may account for the ease with which $\text{Co}(\text{CO})_4$ formation takes place when the iodide is present. By mixing CoBr_2 with powdered Cu, Ag, Au, or Pt and heating with CO under the above conditions, yields up to 82.3 percent were obtained. Copper powder was best.
769. HIEBER, WALTER, AND SEDLMEIER, JOSEF (Technische Hochschule, Munich). [Metal Carbonyls. LXII. The Reaction of Cobalt Tetracarbonyl With Different Bases.] *Chem. Ber.*, vol. 87, 1954, pp. 25-34 (*see* Chem. Abs., vol. 48, 1954, p. 491a); Chem. Abs., vol. 49, 1955, p. 6252b.
770. ——— (Technische Hochschule, Munich). [Carbonyls. LXV. The Reaction of Cobalt Tetra-Carbonyl With Various Types of Bases.] *Chem. Ber.*, vol. 87, 1954, pp. 89-92 (*see* Chem. Abs., vol. 48, 1954, p. 9836e); Chem. Abs., vol. 49, 1955, p. 766f.
771. HIEBER, WALTER, BEHRENS, HELMUTH, AND TELLER, U. [Metal Carbonyls. LXI. The Formation of Iron, Cobalt, and Nickel Carbonyls From the Halides by High-Pressure Synthesis Under Comparable Conditions.] *Ztschr. anorg. allgem. Chem.*, vol. 249, 1942, pp. 26-42 (*see* Chem. Abs., vol. 37, 1943, p. 2293¹); Chem. Abs., vol. 37, 1943, p. 3683².
- When FeI_3 is heated for 15 hr. at 200°-250° C. with CO (200 atmospheres at room temperature) in a Cu-lined vessel a 50- to 75-percent yield of $\text{Fe}(\text{CO})_5$ is obtained, along with a smaller quantity of $\text{Fe}(\text{CO})_4$. Using FeBr_3 or FeCl_3 under the same conditions, only traces of carbonyls are formed. Under the above conditions, nickel and cobalt iodides give almost quantitative yields of carbonyls, but their chlorides and bromides produced only a few percent. The intermediates $\text{Fe}(\text{CO})_4\text{I}$ and $\text{CoI}_2 \cdot \text{CO}$ (*see* Hand Lagolly, Chem. Abs., vol. 35, 1941, p. 7860³) disproportionate readily, forming the pure carbonyl. The formation of the carbonyl is facilitated by using a mixture of the powdered metal and iodine in place of the iodide, since the intermediate compound is then obtained in a finely divided active form. The iodine is regenerated in the reaction. If FeI_3 is mixed with Cu powder before the reaction, the carbonyl is formed at lower temperature. The use of Ag powder in the reactions is also considered.
772. HIEBER, W., KRÄMER, K., AND SCHULTEN, H. [Metal Carbonyls, Metal Carbonyl Hydrides.] *Angew. Chem.*, vol. 49, 1936, pp. 463-464 (*see* British Chem. Abs., 1932, p. A-485 and 1933, p. A-685); British Chem. Abs., 1936, p. A-1080.
- Cobalt tetracarbonyl (3 molecules) reacts with bases yielding Co carbonyl hydride $\text{Co}(\text{CO})_4\text{H}$ (2 molecules) and $\text{Co}(\text{CO})_2$ (1 molecule) with strong bases or $\text{Co}(\text{OH})_2$ (1 molecule) with weak bases. The hydride $\text{Co}(\text{CO})_4\text{H}$ has a melting point of -22° C. and decomposes above -18° C., yielding $\text{Co}(\text{CO})_4$ and H_2 . With complex o-phenanthroline-Ni and -Co ions, it yields the compounds $[\text{Co}(\text{CO})_4]_2[\text{Ni}(\text{C}_6\text{H}_8\text{N}_2)_2]$. With concentrated solutions containing $[\text{Ni}(\text{NH}_3)_6]^+$, it yields the compound $[\text{Co}(\text{CO})_4]_2[\text{Ni}(\text{NH}_3)_6]$. Action of concentrated aqueous NH_3 on $\text{Co}(\text{CO})_4$ yields the compound $[\text{Co}(\text{CO})_4]_2[\text{Ni}(\text{NH}_3)_6]$. Discusses the series relationships of iron, cobalt, and nickel carbonyls and carbonyl hydride and their structures.
773. HIEBER, W., SCHUH, R., AND FUCHS, H. [Metal Carbonyls. XXXVII. Rhenium Halo Pentacarbonyls. Their Tendency of Formation and Properties.] *Ztschr. anorg. allgem. Chem.*, vol. 248, 1941, pp. 243-255 (*see* Chem. Abs., vol. 36, 1942, p. 1256²); Chem. Abs., vol. 37, 1943, p. 3681².
- The high-pressure synthesis of rhenium halocarbonyls from activated Re and anhydrous nickel halides yields also nickel carbonyl:
- $$2\text{Re} + \text{NiCl}_2 + 14\text{CO} \rightarrow 2\text{Re}(\text{CO})_5 + \text{Ni}(\text{CO})_4$$
- The various nickel halides were tested for carbonyl formation with carbon monoxide under pressure in the presence of various metals, including Re. Apparently Re, and to a smaller extent Cu, may act as a catalyst here, as their presence makes for a much improved yield of nickel carbonyl under certain conditions.
774. HIEBER, W., SCHULTEN, H., AND MARIN, R. [Metallic Carbonyls. XXVIII. High-Pressure Synthesis of Cobalt Carbonyl and Cobalt Carbonyl Hydride From Cobalt Compounds.] *Ztschr. anorg. allgem. Chem.*, vol. 240, 1939, pp. 261-272 (*see* Chem. Abs., vol. 32, 1938, p. 3715¹); Chem. Abs., vol. 33, 1939, p. 3285².
- Dry CoS is heated for 12 hr. at 190° C. in CO at a pressure of 250 atmospheres in a rotating autoclave. Well-formed needles of orange yellow $[\text{Co}(\text{CO})_4]_2$ are obtained. Anhydrous CoI_2 in CO at 145 atmospheres for 12 hr. at 160° C. yields quantitative tetracarbonyl, or for a longer time at room temperature. Also $\text{HCo}(\text{CO})_4$ is formed by action of CO and H on dry salts, Co carbonyl, or Co metal.
775. REIFF, F. [Structure and Properties of Tricarbonyl Nitrosyl Cobalt.] *Ztschr. anorg. allgem. Chem.*, vol. 202, 1931, pp. 375-381; Chem. Abs., vol. 26, 1932, p. 1208.
776. REPPE, WALTER, AND OTHERS (Badische Anilin u. Sodafabrik, Ludwigshafen, Germany). [Carbonylation. I. Metallic Carbonyls and Hydrides of Metallic Carbonyls.] *Ann.*, vol. 582, 1953, pp. 116-132; Chem. Abs., vol. 48, 1954, p. 11,312d.
777. SACCO, ADRIANO (University of Milan). (Complex Cobalt-Carbonyl Isocyanide Salts.) *Gazz. chim. ital.*, vol. 83, 1953, pp. 632-636; Chem. Abs., vol. 49, 1955, p. 768h.
778. ——— (University of Milan). [Substitution Products of Cobalt Carbonyl With Trivalent Phosphorous Compounds.] *Ann. chim. (Rome)*, vol. 43, 1953, pp. 495-498; Chem. Abs., vol. 48, 1954, p. 5012d.
779. SCHLECHT, LEO, HAMPRECHT, GÜNTHER, AND SPUN, FRITZ (assigned to I. G. Farbenindustrie, A. G.) [Cobalt Nitrosyl and Nitrosocarbonyl.] German Patent 613,400, May 18, 1935 (*Cl. 12n*); addition to German Patent 566,448 (Chem. Abs., vol. 27, 1933, p. 1106); Chem. Abs., vol. 29, 1935, p. 5600².
- Cobalt or material containing Co is treated at about 150° C. and atmospheric pressure with CO-NO mixtures containing more than 5 percent of NO. Mixtures

containing about 15 percent or more of NO yield Co nitrosyl $[\text{Co}(\text{NO})_3]$, a dark-brown crystalline compound thus can be sublimed in vacuo at about 60°C . without decomposition. CO-NO mixtures containing less than about 15 percent but more than 5 percent of NO yield mixtures of $\text{Co}(\text{NO})_3$ and cobalt nitroso-carbonyl.

780. SEEL, FRITZ. [Metal Carbonyls. LI. A New Method for the Preparation of the Nitrosyl Carbonyls of Cobalt and Iron.] *Ztschr. anorg. allgem. Chem.*, vol. 269, 1952, pp. 40-43; *Chem. Abs.*, vol. 47, 1953, p. 3169b.

Cobalt nitrosyl carbonyl and iron nitrosyl carbonyl are prepared by the acidification of a solution of the alkali salts of the corresponding carbonyl hydrides and an equivalent amount of sodium nitrite. In a specially designed apparatus, 14 grams of cobaltous sulfate heptahydrate in 35 ml. of water, 22.4 grams of potassium hydroxide in 22 ml. of water, 3.2 gm. of potassium cyanide in 5 ml. water, and 20 ml. of water are shaken (after removal of air by carbon monoxide) for 24 hr. with carbon monoxide. This solution, containing the potassium salt of cobalt carbonyl hydride, after addition of 3.5 gm. of sodium nitrite in 10 ml. of water, is added dropwise to 100 ml. of 50-percent acetic acid, which is cooled to 10° to 15°C ., with the exit gases cold-trapped, giving 50 percent of cobalt nitrosyl carbonyl. Directions for producing iron nitrosyl carbonyl and the potassium salt of cobalt carbonyl hydride are given also.

781. SIDGEWICK, N. V., AND BAILEY, R. W. Structures of the Metallic Carbonyl and Nitrosyl Compounds. *Proc. Roy. Soc. (London)*, vol. A-144, 1934, pp. 521-537; *Chem. Abs.*, vol. 28, 1934, p. 4676¹.

782. SMAGINA, E. I., AND ORMONT, B. F. [The Question of Heat of Formation of Nickel Carbonyl.] *Zhur. Obshchei Khim.*, vol. 25, 1955, pp. 224-230; *Jour. Gen. Chem. (U. S. S. R.)*, vol. 25, 1955, pp. 207-212 (English trans.) *Chem. Abs.*, vol. 49, 1955, p. 11,386h.

783. SPICE, J. E., STAVELEY, L. A. K., AND HARROW, G. A. The Heat Capacity of Nickel Carbonyl and the Thermodynamics of Its Formation From Nickel and Carbon Monoxide. *Jour. Chem. Soc.*, 1955, pp. 100-104; *Nuclear Sci. Abs.*, vol. 9, No. 10, 3393, p. 437; *Chem. Abs.*, vol. 49, 1955, p. 6714d.

784. STERNBERG, H. W., FRIEDEL, R. A., AND ORCHIN, MILTON (Bureau of Mines, Bruceton, Pa.). The Chemistry of the Metal Compounds. III. The Reaction Between Dicobalt-Octacarbonyl and Dimethylamine. *Jour. Am. Chem. Soc.*, vol. 75, 1953, pp. 3148-3152 (see *Chem. Abs.*, vol. 47, 1953, p. 4235b); *Chem. Abs.*, vol. 47, 1953, p. 11,063h.

When excess dimethylamine is condensed onto dicobalt octacarbonyl at -80°C . and the mixture warmed to room temperature, a homomolecular disproportiona-

tion appears according to $3[\text{Co}(\text{CO})_4]_2 + 20\text{Me}_2\text{NH} \rightarrow 2[\text{Co}(\text{Me}_2\text{NH})_4]_2[\text{Co}(\text{CO})_4]_2(\text{I}) + 8\text{HCONMe}$. Actually an additional 4 molecules of dimethyl-amine is complexed by the carbon monoxide groups of the dicobalt-octacarbonyl anion. By employing a high partial pressure of CO, the dicobalt octacarbonyl acts as a transfer agent for CO, and only catalytic amounts are required for the carbonylation of dimethyl-amine and piperidine to the corresponding formamides. It was demonstrated that carbon monoxide in metal carbonyls forms complexes with hydrogen bonds. Pyridine and dicobalt-octacarbonyl gave [Copy 6] $[\text{Co}(\text{CO})_4]_2$.

785. SUZUKI, SHIGENARI, ITO, HIROO, TATEMACHI, HIDE-MARO, AND KIMATA, SHIZUO (Toa Gosei: *Chem. Ind. Co.*, Nagoya). [Preparation of Nickel Carbonyl by the Reppe Process. II. Influence of Impurities.] *Jour. Chem. Soc. Japan, Ind. Chem. Sec.*, vol. 54, 1951, pp. 511-513; *Chem. Abs.*, vol. 47, 1953, p. 6297h.

In the preparation of nickel carbonyl from $\text{Ni}(\text{NH}_3)_4\text{Cl}_2$ and CO, the influence of the impurities contained in $\text{Ni}(\text{NH}_3)_4\text{Cl}_2$ has been studied, together with N, H_2 , and O_2 impurities in the CO. The formation is supposed to take place in three stages (1) $\text{Ni}(\text{NH}_3)_4\text{Cl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ni}(\text{OH})_2 + 2\text{NH}_4\text{Cl} + 4\text{NH}_3$; (2) $\text{Ni}(\text{OH})_2 + \text{CO} \rightarrow \text{Ni} + \text{H}_2\text{CO}_3$; and (3) $\text{Ni} + 4\text{CO} \rightarrow \text{Ni}(\text{CO})_4$. When the temperature is constant, the reaction (1) is suppressed by ammonia or ammonium chloride, but the suppression is compensated by elevation of temperature. Reactions (2) and (3) are disturbed by oxygen, but not noticeably by nitrogen or hydrogen.

786. WENDER, I., STERNBERG, H. W., AND ORCHIN, M. (Bureau of Mines, Bruceton, Pa.). Evidence for Cobalt Hydrocarbonyl as the Hydroformylation Catalyst. *Jour. Am. Chem. Soc.*, vol. 75, 1953, pp. 3041-3042 (see *Chem. Abs.*, vol. 47, 1953, p. 6895e); *Chem. Abs.*, vol. 48, 1954, p. 1125c.

Dicobalt octacarbonyl in pyridine treated at 120°C . and 230 atmospheres with synthesis gas (a mixture of H_2 and CO) yielded $[\text{C}_5\text{H}_5\text{NH}]^+[\text{Co}(\text{CO})_4]^-$ (1). This was also prepared by adding pyridine to $\text{HCo}(\text{CO})_3$ at room temperature. Pure $\text{HCo}(\text{CO})_3$ in the absence of CO and H_2 reacts with cyclohexane, 1-hexene, $\text{PhCMe}:\text{CH}_2$, PhCH_2OH , benzhydrol, and Ph_3COH at room temperature and 1 atmosphere to give the same products as given from the same substances under hydroformylation conditions.

787. WILSON, E. B., JR. Normal Frequencies of Vibration of the Plane Square Molecule AB₃ With Reference to the Structure of Nickel Carbonyl. *Jour. Chem. Phys.*, vol. 3, 1935, p. 59; *British Chem. Abs.*, 1935, p. A-284.

The model AB₃ is treated analytically, and the results are given. The method used by Duncan and Murray (*British Chem. Abs.*, 1934, p. A-1289) is criticized.

PART III. HYDROMETALLURGICAL

HYDROMETALLURGY; GENERAL

788. SHELTON, F. K., CHURCHWARD, R. E., STAHL, J. C., AND LIVINGSTON, G. F. (Bureau of Mines, Boulder City, Nev.). Study of Certain Factors in the Hydrometallurgy and Electrodeposition of Cobalt. Bureau of Mines Rept. of Investigations 3832, 1945, 43 pp.; Chem. Abs., vol. 40, 1946, p. 3683⁷.

The process is applied to ores containing Co as oxide. It consists of leaching the ore with H_2SO_4 and H_2SO_4 . The Co solution passes through one or more precipitation stages to remove Fe and elements of the Cu group. Cobalt carbonate is precipitated under carefully controlled pH (7.2) conditions and the precipitate dissolved in an acid electrolyte containing H_2SO_4 , H_3BO_3 , and NaF. The electrolysis is conducted in an open cell (zinc type), and the acid concentration is not allowed to increase beyond pH 1.0–1.5. The electrolyte normally contains per liter: 20 gm. of Co, 50 gm. of H_3BO_3 , and 5.0 gm. of NaF. Co can be leached from cobalt ferrites or cobalt arsenates. In the latter instance, a more concentrated H_2SO_4 must be used. The As is precipitated as $FeAsO_4$ (pH 3.45) by adding Na_2CO_3 to the solution. If necessary $Fe[As Fe_2(SO_4)_3 + H_2O]$ is added. The Co, free from As, is precipitated by adding more Na_2CO_3 (pH above 6.45). The influence of pH on precipitation of impurities and of Co and the conditions of the electrolysis electrolyte at different temperatures are discussed.

789. VAN ARSDALE, G. D. (The Door Co.). Hydrometallurgy of Base Metals. McGraw-Hill Book Co., Inc., New York, N. Y., 1953, 370 pp.

Among the 10 chapters in this volume are those on Chemistry of Roasting and Leaching, Crushing, Grinding, Classification, Roasting Practice, Leaching and Solution Separation, and Solution Purification and Metal Recovery. The techniques of materials handling for other metals may be profitably applied in some instances to the hydrometallurgy of nickel and cobalt. A short description of the plant of the Nicaro Nickel Co. in Oriente Province, Cuba, is to be found on pp. 270–274, including topics flowsheet, crushing and drying, grinding, leaching, recovery, and problems.

HYDROWINNING NONSPECIFIED ORES REDUCTION TO METAL

790. CHEMICAL AND ENGINEERING NEWS. Chemical Ore-Reduction Processes May Pay Out in Three Years. Vol. 30, May 19, 1952, pp. 2104–2105; Chem. Week, vol. 70, May 17, 1952, pp. 43, 44, and 46; Steel, vol. 130, May 26, 1952, pp. 76–77. Metals Rev., vol. 25, No. 6, June 1952, p. 24, items 78-C, 79-C; No. 7, July 1952, p. 27.

A new high-temperature, high-pressure all-chemical process for recovering Ni, Co, Cu, and Mn from ore or scrap has just been announced by the Chemical Con-

struction Co., a subsidiary of American Cyanamid. Ore concentrates are made by conventional flotation methods, then leached in H_2SO_4 under pressure to oxidize the S to sulfate. The gangue is filtered out along with the insoluble As compounds and a cation-exchange reaction or cementation step removes the Cu salts. The solution is made ammoniacal and reduced with H_2 under pressure. By altering temperatures and pressures of the reduction it is possible to bring down one metal at a time in the order of their appearance in the electromotive series. It is believed impractical to recover any metal above Zn in the electromotive series. Three refineries are being built to utilize the process.

791. CHEMICAL CONSTRUCTION CO. New Chemical Process Recovers Nickel, Cobalt, and Copper. Min. Eng., vol. 4, No. 6, June 1952, pp. 565–567; Jour. Metals, vol. 4, No. 6, June 1952, pp. 589–591; Min. World, vol. 14, No. 8, July 1952, pp. 44–45; Eng. and Min. Jour., vol. 153, No. 6, June 1952, pp. 84–87; Chem. Eng., vol. 59, No. 6, June 1952, pp. 164–168, 368, 370, 372–374, and 376; Western Mach. and Steel World, vol. 43, No. 9, September 1951, pp. 89–90; Metals Rev., vol. 25, No. 8, August 1952, p. 23 (10-C); Eng. Index, 1952, p. 624.

A process developed by the Chemical Construction Co. involves treatment of oxide and sulfide ore concentrates by chemical methods; simultaneous recovery of Ni, Co, and Cu is accomplished in autoclaves. The Co refinery for Howe Sound Mining Co. near Salt Lake City is expected to raise world Co production 40 percent. Steps in this application of the process are: (1) Acid oxidation leach; (2) filtration; (3) cementation (for Cu removal); (4) reduction from ammoniacal solution; (5) separation of Co and Ni as mixed metals (95 percent Co and 5 percent Ni); and (6) recovery of $(NH_4)_2SO_4$.

792. SCHAUFFELBERGER, F. A. (Chemical Construction Corp., New York). Metal Precipitation From Salt Solution by H_2 Reduction. Prep. of paper to be presented at Annual Meeting of AIME, Chicago, Ill., Feb. 14–17, 1955.

“ABSTRACT: After reviewing some earlier publications on chemical precipitation of metals from metal salt solutions, the chemistry and thermodynamics of precipitating copper, nickel, cobalt, and cadmium metals by reaction with hydrogen are discussed. Experimental data on the following systems are presented: High-purity copper powder from H_2SO_4 and from ammoniacal sulfate solution; high-purity nickel and cobalt powders from H_2SO_4 and from ammoniacal sulfate solution; and cadmium powder from cadmium acetate in alcohol solution.”

793. ——— (assigned to Chemical Construction Corp.). Separation of Nickel and Cobalt Metal From Acidic Solution. U. S. Patent 2,694,005, Nov. 9, 1954; Chem. Abs., vol. 49, 1955, p. 2287g, h, i.

High-purity Co is separated hydrometallurgically from acidic solutions containing Co and Ni and is substantially free from Cu and Fe. The pH is adjusted to acidic conditions with an acid content of approximately 5 percent, and the solution is heated to above 250° F. in the presence of a nonsulfiding reducing gas and a compatible electrolyte, whereby the anion of the

electrolyte forms a gas-reducible anion complex with the Ni ion and the Ni is reduced to Ni metal. The reduction is continued in the presence of a soluble-salt-forming, acid-neutralizing agent, which, after reduction, produces a pH of 0.1-0.2 percent for original Ni : Co mol. ratios of 5 : 1 and concentrations up to 1 percent for Ni : Co ratios of 1 : 1 to 1 : 10. When the Ni precipitation ceases, the precipitate is removed, and a solution suitable for Co metal precipitation is obtained. A solution is prepared by dissolving, in 0.2 part aqueous H_2SO_4 , approximately 0.5 part $(NH_4)_2SO_4$, and 0.75 part of a cobalt sulfate mixture having a Ni : Co ratio of 1 : 1. The solution is transferred to a stirred autoclave and heated to 400° F. with the pressure raised to 800 p. s. i. in H_2 ; NH_3 is added to produce 0.5 percent free acid after reduction. After 30 minutes the treatment is stopped, the pressure is relieved, and the solids are collected. The filtrate is re-treated under similar temperature and pressure after neutralization of the free acid with added NH_3 . In the first product the Ni powder contains approximately 2.5 percent Co, and the second contains approximately 97 percent of the original Co with 2.3 percent Ni. Purer materials are obtained by carrying the reductions to a lower cutoff acidity of 0.2 percent free acid.

794. SCHAUFELBERGER, F. A., AND MCGAULEY, P. J. (assigned to Chemical Construction Corp.). Separation of Nickel and Cobalt Metal From Amine Solution. U. S. Patent 2,694,006, Nov. 9, 1954; Chem. Abs., vol. 49, 1955, p. 2288a.

Substantially Ni-free Co is separated from a mixture containing both metals by precipitating from an aqueous solution containing dissolved Co and Ni at from 275° to 400° F., and then treating with a non-sulfidizing reducing gas and a complex-forming amine to produce a solution of molecular ratio of unneutralized amine to dissolved Co plus Ni of approximately 1.5 : 4. The Ni metal powder is precipitated and removed. Ammonia is added to the residual solution to produce an amine: dissolved-Co ratio above 4. Cobalt is precipitated by further reduction at a higher temperature and is collected. One part of a crystal mixture of cobalt and nickel sulfides having a Ni : Co ratio of 4 : 5, which had been previously treated to recover Cu, is dissolved in H_2O with 1.2 parts of $(NH_4)_2SO_4$. The acidity of the solution is about pH 4.5. The slurry is transferred to a stirred autoclave and treated with 100 gm. per l. of Ni powder, 2 moles of NH_3 per mole of metal, and enough H_2 to maintain a pressure of 800 p. s. i. at 350° F. Treatment at 320°-400° F. is conducted for ½ hr. Up to 40 percent of the Ni is precipitated as metal powder containing less than 2 percent Co. In a second treatment, by using up to 0.5 additional part of NH_3 , most of the remaining Ni is coprecipitated with Co at 350°-425° F. In a third treatment, above 400° F., approximately 40-50 percent of the Co is recovered in a fraction containing 3-6 percent of Ni. Substituted amines, such as ethylamine or ethyldiamine, can be used in place of NH_3 .

795. TRONEV, V. G., BONDIN, S. M., AND KRENOVA, A. L. [Reduction of Cobalt, Nickel, and Copper From Complex Compounds With Hydrogen Under Pressure.] Izvest. Sektora. Platiny i Drugikh Blagorod. Metal Inst. Obshchei i Neorg. Khim. Akad. Nauk, S. S. S. R., vol. 23, 1949, pp. 123-131; Chem. Abs., vol. 45, 1951, p. 2359h.

The complexes, $Co(NH_3)_6SO_4$ (2 gm.), $Ni(NH_3)_6SO_4$ (1.2 gm.), and $Cu(NH_3)_4SO_4$ (3 gm.) were separately placed in 100 ml. of water containing 24-25 percent of free NH_3 at 20°-200° C. and 50 to 75 atmospheres of H_2 pressure. The solutions were stirred vigorously. The quantity of reduced metal in each of the solutions was determined. At 100° C. no metal had appeared. At 125° C. all 3 metals were reduced, but to a different extent, Cu most, Co least. At 175° C. all of the Cu

and Ni was reduced, and at 200° C. Co was completely reduced in 2 hours. Heating $Co(NH_3)_6Cl_2$ under 50 atmospheres of H_2 gave complex results in which hydrolytic and reduction reactions occurred. Addition of NH_4OH and NH_4Cl to purpureo salt $[Co(NH_3)_6Cl_2]$ heated at 200° C. under 50 atmospheres of hydrogen arrested reduction and solubilized hydrolysis products. Attempts at selective precipitation of Co and Ni from their hexamine chlorides at elevated temperatures and hydrogen pressure were unsuccessful.

796. WALDRON, H. L. Sheritt Gordon Develops Lynn Lake Nickel-Copper. Eng. and Min. Jour., vol. 152, No. 11, 1951, pp. 72-78; Chem. Abs., vol. 46, 1952, p. 387h.

A new development of this Manitoba property has been the discovery of blind ore bodies, successful use of electromagnetic surveying, addition to sulfide Ni reserves, and a new Ni concentration by leaching and precipitating Ni and Co as powders.

797. WATT, G. W., AND KEENAN, C. W. Reduction of Certain Cobalt Salts in Liquid Ammonia. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 2048-2050; British Abs., 1952, p. A-I-800.

In the reaction with K in liquid NH_3 , $Co(NO_3)_2$ is converted to $Co(NH_3)_6$, with simultaneous reduction of NO_3^- to NO_2^- . $Co(NH_3)_6$ and $CoBr_2$ are reduced to Co.

LEACHING

798. BARABOSHKIN, N. N., BERENOV, S. V., AND SHAROVA, A. K. [The Hydrometallurgy of Low-Grade Nickel Ores.] Uralskii Gosudarst. Nauk. Issledovatel. Inst. Tsvetnye Metal. Sbornik Nauk-Issledovatel. Rabot No. 1, 1935, pp. 74-85; Chem. Abs., vol. 31, 1937, p. 3839^g.

The ores are treated with H_2SO_4 , dried, and heated at about 700° C. Extraction with hot water removes Ni along with Fe and Al, which are precipitated with calcium carbonate. The Ni is precipitated with sodium sulfide. Individual ores require some modification of this general procedure.

799. CADENHEAD, A. F. Advances in Chemical Metallurgy. Canadian Chem. Proc., vol. 37, No. 5, 1953, pp. 38-40; Chem. Abs., vol. 47, 1953, p. 6321a.

The production of liquid SO_2 , oxidation and NH_3 leaching of Ni-Co-Cu ores, subhalide distillation of Al, and the production of electric pig iron and TiO_2 from ilmenite are discussed.

800. CARRERAS, R. S. Cobalt From Complex Ores. U. S. Patent 1,928,340, Sept. 26, 1933; Swedish Patent 145,490, July 10, 1929 (Chem. Abs., vol. 26, 1932, p. 37); French Patent 677,720, July 2, 1929 (Chem. Abs., vol. 24, 1930, p. 3206^g); British Patent 336,584, July 10, 1929 (Chem. Abs., vol. 25, 1931, p. 1789^g); Chem. Abs., vol. 27, 1933, p. 5655.

Ores such as those containing Co with Cu and alkaline-earth gangue are subjected to the action of H_2SO_4 and NaCl to attack the metals of the ore, and the solution thus obtained is electrolyzed by the use of unattackable anodes, such as graphite and thin sheet-Cu cathodes, until all the Cu has been eliminated; the electrolyte is then concentrated by evaporation to favor precipitation of alkaline-earth salts, the liquid is filtered, further concentrated, and cooled in order that the content of Co may separate as cobalt sulfate crystals; the separated cobalt sulfate is then dissolved, and the solution so formed is electrolyzed to obtain metallic Co.

801. CHEMICAL CONSTRUCTION CO. New Ore-Treatment Process. Canadian Chem. Processing, vol. 36, No. 10, September 1952, pp. 58 and 60; Eng. Index, 1952, p. 723.

A leaching process offers many advantages for eco-

conomic recovery of Lynn Lake, Alberta, ores not to be found in normal smelting and refining techniques. The new Sherritt Gordon plant using this process will produce annually 8,500 tons of Ni, 1,000 tons of Cu, 150 tons of Co, and 70,000 tons of $(\text{NH}_4)_2\text{SO}_4$ and many useful byproducts. A flow plan is included.

802. COMSTOCK & WESTCOTT, INC. [Nickel Ores.] French Patent 775,161, Dec. 21, 1934; Chem. Abs., vol. 29, 1935, p. 2139².

Ores containing Ni and Fe are treated in the nearly dry state with hydrochloric-acid gas and steam at low temperatures (180° – 300° C.), regulating the gas-steam ratio and the temperatures. The nickel chloride is leached out with water.

803. COOPER, R. A., AND WATSON, F. W. The Development of the "Chlorine Process" of Extraction of Platinum Metals From Ore. Jour. Chem. Met. Min. Soc. South Africa, vol. 29, 1929, pp. 220–230; Chem. Abs., vol. 23, 1929, p. 4656¹.

Various methods of concentration and leaching with various solvents were tried on an ore containing Pt, Cu, Ni, and Co from the Waterberg district, Transvaal. Only cyanide and Cl_2 gas gave encouragement. The application of Cl_2 was tried in various ways, and finally 80-percent extraction was obtained by heating the ore to 550° C. in a glass combustion tube and passing moist Cl_2 through, then leaching with acidified H_2O . The addition of 1 percent NaCl increased extraction to 90 percent. A revolving steel tube of large capacity gave good results on original ore and tailings, but the costs were too high for low-grade material, and on concentrates the results were poor. Similar treatment, using a stationary rectangular muffle, however, was successful, unless coarse Pt was present. In this case, electrolytic amalgamation (*see* Chem. Abs., vol. 23, 1929, p. 3194) was used, followed by chlorination of the tailings, yielding 90-percent extraction. On norite, ore flotation was the only successful method of concentration. By this, 87 percent of the Pt was obtained in 5 percent of the ore, but the previous method could not extract the Pt from this concentrate because Pt existed as a solid solution or submicroscopic dispersion within base-metal sulfides in the ore. A slight modification in roasting, with elimination of NaCl, then resulted in successful chlorination and leaching without amalgamation. From the solution obtained, Pt is precipitated with Zn dust. Copper must be precipitated before precipitation of Co, slow precipitation with pulverized limestone being found best. Nickel remains after the Pt is precipitated and is then precipitated separately. Thus 80 percent of the Cu and Ni in the ore is recovered, besides the Pt. The final product carries 52 percent Pt and 15 percent Pd. A commercial plant has been built and is treating flotation concentrates from sulfide norite carrying 25–30 dwt. of Pt per ton.

804. DU FAUR, J. B. Recovery of Cobalt or Nickel (or both) and Copper From Ores Containing Them. Australian Patent 22,703, Sept. 27, 1929; Chem. Abs., vol. 25, 1931, p. 5383.

The metal contents of the ores are dissolved as chlorides or sulfates. The solution is treated with cobalt carbonate or hydrate, whereby the Cu is precipitated. The Co and/or Ni solution is treated in the usual manner.

805. FORWARD, F. A. Alkaline Pressure-Leaching Process. Min. Cong. Jour., vol. 40, No. 5, May 1954, pp. 49–52 and 77; Eng. Index, 1954, p. 758; Metals Rev., vol. 27, No. 7, p. 28 (185–B).

Operation at high pressures and temperatures speeds reactions and permits difficult separations with great economies in equipment and reagents. The ammonia-leach process and uranium-ore treatment are discussed.

806. FOSSET, H. E. [Nickel.] French Patent 663,347, July 3, 1928; Chem. Abs., vol. 24, 1930, p. 582².

Ni ores are decomposed by heating to dryness with 25° B. H_2SO_4 , removing the water-soluble portion containing Fe, Ni, and Mg, which when treated with NH_3 gives a special Ni. The filtrate is again evaporated with dilute H_2SO_4 and gives Fe–Ni. SiO_2 is obtained from the residue.

807. GEBRÜDER BORCHIERS, A. G., AND BORCHIERS, FRIEDRICH. [Treating Cobalt Ores.] German Patent 505,229, Jan. 24, 1929; Chem. Abs., vol. 24, 1930, p. 5709².

Argentiferous Co ores or metallurgical products are heated with H_2SO_4 of more than 40° B. under a pressure of 4 atmospheres or more, preferably 8 to 10 atmospheres. The Co is thus dissolved, but Ag remains undissolved. Ore containing much S should be preliminarily roasted. Examples are given.

808. GROTH, HANS (assigned to Metallhütte Magdeburg G. m. b. H.) [Working Up Cobaltiferous Sludge.] German Patent 518,901, Jan. 20, 1928; Chem. Abs., vol. 25, 1931, p. 3304¹.

The sludge, especially that from the treatment of roasted pyrites with CaCl_2 , is first treated with 5 percent HCl to remove Zn and then fractionally leached out with H_2SO_4 to dissolve the Co. The Fe, Cu, and Zn present are removed by precipitation in known manner, and the Mn is removed by fractional precipitation with HClO_4 . The sludge is preferably heated in the presence of air before treatment.

809. KARASHIMA, YUSURU, AND KAMATA, MINORU (assigned to Mitsubishi Chemical Industrial Co.). [Treatment of Nickel-Containing Substance.] Japanese Patent 175,770, Mar. 11, 1948; Chem. Abs., vol. 44, 1950, p. 8309g.

The concentration of H_2SO_4 in 100 gm. of solution containing Ni should be 40 to 70 gm. for the extraction of Ni from Co and other impurities Zn, Mn, and Fe and at a temperature below 50° C.

810. KONINKLYKE ZWAVELZUURFABRIEKEN VOORHEEN KETJEN N. V. [Selective Extraction of Copper, Nickel, and Cobalt From Their Ores, Simultaneously Winning Alkaline-Earth Nitrates.] Netherlands Patent 52,158, Mar. 16, 1942; Chem. Abs., vol. 41, 1947, p. 3736g.

Extraction is performed with nitrous gases, air, and steam and made selective by regulating the temperature of the extraction by cooling.

811. MCGAULEY, P. J. (assigned to Chemical Construction Co.). Recovery of Complex Ammonium Sulfates From Mineral Leach Liquors. U. S. Patent 2,647,819, Aug. 4, 1953; Chem. Abs., vol. 47, 1953, p. 10,448c.

Cu and Co are recovered from concentrates that may also contain Ni and Fe by leaching with H_2SO_4 or an ammoniacal liquor, filtering, adjusting the pH of the filtrate to 3 to 4 to precipitate $\text{Fe}(\text{OH})_3$, increasing the pH to 4 to 6.4 to precipitate nickel ammonium sulfate, increasing the ammonium-salt concentration to about 40 percent at a pH of about 5.5 to precipitate Co as a complex ammonium sulfate, and increasing the ammonium-salts concentration to greater than 50 percent to precipitate Cu as a complex ammonium sulfate. S may be recovered from the precipitated solids by melting, filtering, and cooling. The metals may be recovered from the sulfates by roasting and reduction.

812. MEYER, R. M. (assigned to Meyer Mineral Separation Co.). Recovering Metal Values From Oxidized and Nonsulfide Ores Such as Those of Iron, Copper, Nickel, etc. U. S. Patent 1,900,299, Feb. 5, 1935; Chem. Abs., vol. 29, 1935, p. 1766².

After partial reduction, the ore is made partly wet

by a solubilizing agent such as FeCl_3 solution and allowed to remain to effect solubilizing for some time, before the values are recovered from the ore.

813. MITSUBISHI COTTON INDUSTRIES Co. [Purification of Nickel Sulfate.] Japanese Patent 155,522, Mar. 17, 1943; Chem. Abs., vol. 43, 1949, p. 6376f.

From an H_2SO_4 solution of nickeliforous Fe ores, the sulfates of Fe, Mn, Cu, Co, and other metals were precipitated by heating to $125^\circ\text{--}135^\circ\text{C}$. and stirring vigorously for 20 minutes. A very pure, slightly hydrated nickel sulfate precipitated when the solution was kept at $150^\circ\text{--}155^\circ\text{C}$. for 20 minutes. By utilizing the filtrate repeatedly for making the solution of the ores, almost all of the Ni was extracted.

814. NATIONAL PROCESSES, LTD., AND GIBSON, A. R. Leaching Ores, etc. British Patent 349,563, Nov. 29, 1929; Chem. Abs., vol. 26, 1932, p. 1890.

Various metalliferous materials, such as those containing Zn, Cu, V, Ni, Co, and other metals, are leached with neutral, acid, or basic solutions containing NH_3 and SO_2 without application of external heat and with exclusion of air or other oxidizing agents. Metals are recovered from the solutions obtained by various methods.

815. SCHLEA, C. S. (Ohio State University). Extraction of Iron, Cobalt, and Nickel Sulfates. Columbus Univ. Microfilms (Ann Arbor, Mich.), Pub. 12,189, 159 pp.; dissertation abs., vol. 15, 1955, pp. 971-972; Chem. Abs., vol. 49, 1955, p. 12,167g.

816. SCHOPPER, WALTER (assigned to Norddeutsche Affinerie). [Nickel, Cobalt, etc.]. German Patent 545,836, Sept. 10, 1930; Chem. Abs., vol. 26, 1932, p. 3476.

Ni, Co, etc., or their salts are obtained from ores or foundry products by first subjecting them to a dry concentration process by which Cu, Pb, Fe, and noble metals are removed and a Co-As or Co-Sb or a Ni-As or Ni-Sb mass is formed. The latter is then separated and treated with H_2SO_4 to produce NiSO_4 or CoSO_4 and H_2AsO_4 or H_2SbO_4 . The NiSO_4 or CoSO_4 is then leached out with water, the acids remaining in the residue. The salt solution may be concentrated and the metal obtained, if desired, by the usual methods. Examples are given.

817. SMITH, S. C. Treating Nickeliforous Materials. U. S. Patent 1,770,866, July 15, 1930 (see British Patent 311,909; Chem. Abs., vol. 24, 1930, p. 816); Chem. Abs., vol. 24, 1930, p. 4501⁴.

818. SMURNOV, A. A. [Extracting Nickel From Low-Grade Ores.] Russian Patent 39,393, Oct. 31, 1934; Chem. Abs., vol. 30, 1936, p. 3393⁴.

The ores are extracted with HCl , Fe is removed from the solution by known methods, such as treatment with MgO , or CaCO_3 , and the salts (after evaporation to dryness) are hydrolyzed with steam superheated to $350^\circ\text{--}400^\circ\text{C}$. Ni is then extracted from the mixture by usual metallurgical methods, while the HCl vapors are recirculated for extraction of values from new ore.

819. STENDER, V. V. [Chemical and Electrochemical Methods in the Metallurgy of the Nonferrous Metals.] Jour. Appl. Chem., U. S. S. R., vol. 19, 1946, pp. 231-243; Chem. Abs., vol. 41, 1947, p. 64f.

Gives résumé of results obtained in six projects started in connection with local deficiency of chemical supplies. Co is extracted from Ni-free ores in a hydrometallurgical operation. A study of the electrical conductivity of mixtures of aqueous solutions used in electrolysis concerns the effect of Fe and Cu on the conductivity of nickel bisulfate. Includes bibliography.

820. TAFEL, V., AND LAMPE, G. [Extraction of Nickel From Frankenstein Nickel Ores.] Metallwirtschaft, vol. 16, 1937, pp. 721-725 (see Chem. Abs., vol. 32, 1938, p. 89⁴); Chem. Abs., vol. 32, 1938, p. 4494⁴.

Leaching with hot 3- to 4-percent H_2SO_4 dissolves 90 percent of the Ni and 72 percent of the Fe in the ore. Various alkaline and salt solutions are ineffective. Treatments with Cl_2 at 250°C . convert most of the Ni but little of the Fe into a water-soluble form. Heating for several hours at 650°C . with gases from a roasting furnace (SO_2 plus air) enriched with approximately 0.5 percent of O_2 has a similar effect and is cheaper.

821. URAZOV, G. G., AND ROMANOV, M. M. [Hydrometallurgical Treatment of Ural Nickel Ores.] Tsvetnye Metal, vol. 5, 1930, pp. 1136-1144; Chim. et ind., vol. 25, 1931, pp. 619-620; Chem. Abs., vol. 25, 1931, p. 3281⁴.

Ni is generally extracted from its oxide ores by treatment with acid; but with low-grade ores the acid consumption is high because of the large proportions of easily soluble Fe, Mg, and Al oxides. Neutral or alkaline solvents are not used on account of their low solvent power. Urazov and Romanov studied the attack of washed ores containing 0.9-5.68 percent Ni by means of a solution of SO_2 or by SO_2 gas; extraction of Ni is possible in both cases. The yield increases with the concentration of SO_2 in solution and with the time of treatment. In treatment with SO_2 gas the yield increases with the amount of wash water but is independent of the time of treatment. SO_2 gas acts by being oxidized to SO_3 , the oxidation being accelerated by the presence of certain substances, such as FeSO_4 .

822. WESTBY, H. C. Leaching Ores Containing Copper and a Ferruginous Gangue Carrying Siliceous Material. U. S. Patent 2,357,715, Sept. 5, 1944; Chem. Abs., vol. 40, 1946, p. 7145⁴.

An ore containing Cu, Zn, Mn, Al, Ni, Co, and Cr is treated with a NaHSO_3 solution and a retardant of oxidation, such as alcohol, sugar, starches, or SnCl_4 , so that a solution is produced containing soluble Na_2SO_3 and also a mass containing the ore gangue and insoluble sulfites, sulfates, and hydrates of the metallic elements, depending on the constituents and reaction conditions. The regeneration of Na_2SO_3 with counter-currently blown SO_2 precipitates the metallic sulfite of treated ore which is removed by decantation. The residual sulfite is roasted and recovered, from the insoluble mass, while the insoluble mass from the first step is treated further with NaHSO_3 .

PRECIPITATION AND SEPARATION

823. BALINT, ISTVAN. [Separation of Copper and Nickel.] Hungarian Patent 139,995, Sept. 24, 1949; Chem. Abs., vol. 44, 1950, p. 5790f.

Copper and Ni are dissolved as sulfates. Most of the Cu is crystallized as CuSO_4 ; the remaining part is precipitated by the addition of a slight excess of alkali, such as Na_2CO_3 , to give a pH of 6.4. This precipitate is separated, and Ni remaining in the solution is worked up by known methods.

824. BEVERINI, RAOUL, AND RAYMOND, ELIE. [Separating Nickel and Cobalt.] French Patent 786,810, Sept. 10, 1935; Chem. Abs., vol. 30, 1936, p. 715⁴.

Ni and Co are separated by utilizing the fact that they form complex compounds with ethanalamines in alkaline medium, the Co compounds being very stable whereas those of Ni are unstable even in the cold, hydrolyzing to form the hydroxide. Under the same conditions Mn does not give a complex and precipitates immediately as hydroxide (see French Patent 786,868, Sept. 11, 1935). Glycerylamines are used instead of ethanalamines to separate Ni, Co, and Mn, the Ni forming an unstable and the Co a stable complex, while the Mn is precipitated immediately as the hydroxide.

825. CARON, M. H. [Nickel and Cobalt.] French Pat-

ent 837,609, Feb. 15, 1939 (*see* Netherland Patent 44,768); Chem. Abs., vol. 33, 1939, p. 4183^a.

826. CARON, M. H. [Separating Cobalt From Nickel.] Netherland Patent 52,788, July 15, 1942; Chem. Abs., vol. 41, 1947, p. 3736h.

From a solution containing Ni, Co, NH_3 , and $(\text{NH}_4)_2\text{CO}_3$ the metals are precipitated on heating. The precipitate is treated with ammonia or ammonium carbonate solution (at least 5 mols. NH_3 : 1 mol. CO_2) to dissolve the precipitate except the main bulk of Co (*see* Netherland Patent 55,376, Oct. 15, 1943). To precipitate basic nickel carbonate from a solution containing Ni, Co, NH_3 , and CO_2 the solution is evaporated until a precipitate appears, cooled, CO_2 introduced, and the resulting precipitate separated from the liquid. By repeating this process thrice, a solution containing Ni 0.701, NH_3 1.27, CO_2 1.38, SO_4 0.136, and Co 0.036 percent was converted into one with Ni 0.077, NH_3 0.38, CO_2 0.92, SO_4 0.132, and Co 0.036 percent. Thus, about 89 percent of the original Ni content was obtained as a basic carbonate containing little Co.

827. ———. Separating Nickel and Cobalt in Solutions. U. S. Patent 2,290,313, July 21, 1943; Chem. Abs., vol. 37, 1943, p. 5064.

A solution containing Ni, Co, NH_3 , and CO_2 is heated and concentrated until the precipitating basic nickel carbonate starts to contain Co when the operation is stopped. The basic nickel carbonate is separated in substantially pure form.

828. ———. [Separating Nickel and Cobalt.] French Patents 931,701, Mar. 2, 1948, and 931,765, Mar. 3, 1948 (*see* Chem. Abs., vol. 41, 1947, p. 3736h, and vol. 42, 1948, p. 6679b); Chem. Abs., vol. 43, 1949, p. 8109a.

An aqueous solution containing only NH_3 , CO_2 , Ni, and Co is evaporated in stages; the first precipitates contain very high proportions of basic nickel carbonate and only small percentages of the total Co present. By repeating this procedure several times, the Co content can be raised considerably, effecting a separation.

829. ——— (Delft University, Netherlands). [Separation of Nickel and Cobalt.] Jour. Metals, vol. 188, 1950, No. 1, Trans., pp. 91-103; Chem. Abs., vol. 44, 1950, p. 1862h.

Starting with complexes of Ni and Co in an aqueous solution with NH_3 and CO_2 , several processes were tried, based primarily on the greater solubility of Co as the ratio of CO_2 to NH_3 increased: (1) As the NH_3 is expelled, a basic nickel carbonate containing Co is precipitated, and by leaching this with liquors with a low CO_2 : NH_3 ratio, Ni can be redissolved, preferentially to Co. As this process is repeatedly performed, the final residue will be greatly enriched in Co. (2) A selective precipitation from the Ni and Co complex solution precipitates Ni first, with the later precipitates carrying more of the Co. The same result may be achieved by passing CO_2 through the solution during distillation, in which NH_3 is expelled faster than CO_2 . (3) With a starting liquor containing equal concentrations of NH_3 and CO_2 , a distillation is stopped just before the point of incipient nickel carbonate precipitation. A current of CO_2 passed through the cooled solution will precipitate a fairly pure Ni salt, with Co remaining in solution. The cycle may be repeated. Also, (4) the solution may be diluted with water, before the passage of CO_2 , resulting in a heavier precipitation of nickel carbonate.

A material enriched in Co by one of the above schemes may be treated with an acid, dissolving both metals in the bivalent state. If an excess of NH_3 is introduced, soluble complexes will be formed with Ni remaining in the bivalent state, but contact with air will oxidize Co to a brown and finally a dark-red color. $3\text{CoCl}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 10\text{NH}_3 \rightarrow 2\text{Co}(\text{NH}_3)_5\text{Cl}_3 +$

$\text{Co}(\text{OH})_2$.] If enough NH_4Cl is present cobalt will remain in solution, but without it one-third of the cobalt will precipitate. The use of H_2O_2 will hasten the above reaction.

With Ni and Co present as complexes in aqueous NH_3 solutions, the passage of an electric current will plate out Ni more readily.

Directions for the above processes and tables are included.

830. CHEMICAL CONSTRUCTION CORP. Hydrometallurgy of Nickel and Cobalt. British Patent 719,280, Dec. 1, 1954; Chem. Abs., vol. 49, 1955, p. 5255i.

Cobalt is recovered from a nickel-cobalt sulfate solution by adjusting the SO_4 : Co ratio to at least 3 : 2 with the SO_4 : Ni ratio to 1. The solution is saturated with NH_3 and oxidized with S-free O_2 or air at 200°-300° F. and a total pressure at least equivalent to the vapor pressure of the solution, to precipitate a trivalent cobalt ammine compound. The mixture is filtered to recover the cobalt compound.

831. DE MERRE, MARCEL (assigned to Société générale métallurgique de Hoboken). Separation of Nickel From Solutions Containing Cobalt and Nickel. British Patent 683,679, Dec. 3, 1952; Chem. Abs., vol. 47, 1953, p. 4274b.

Ni and Co together can be separated from solutions of their sulfates, chlorides, or other soluble salts from the metals Zn, Fe, Mg, and Mn. With pH between 1 and 5.5 and with agitation at 85° C., powdered metallic Co and S, As, Sb, Te, or Se powder are introduced. The presence of Fe, Zn, Mg, Cu, or Pb does not hinder the precipitation. Fe, Zn, and Mn remain in solution with the Co; the Cu and Pb are precipitated with the Ni.

832. ——— (assigned to Société générale métallurgique de Hoboken.) An Improved Process for the Separation of Cobalt and Nickel. U. S. Patent 2,651,562, Sept. 8, 1953 (*see* British Patent 655,149; Chem. Abs., vol. 46, 1952, p. 2987d); Chem. Abs., vol. 47, 1953, p. 6837i.

Nickeliferous cobalt alloys and other metallic substances are treated for approximately 4 hr. at 95° C. with a dilute acid, either H_2SO_4 or HCl , at pH of 1.5 to 5.5, in the presence of S, Se, As, Te, or Sb to convert Ni to an insoluble form and Co to a soluble form. S is the preferable element. The presence of Fe is beneficial, and an alkyl sulfonic wetting agent may be added. If Cu is present it is precipitated as a sulfide, and any Zn or Mn present is soluble with the Co.

833. DYSON, G. M. The Extractions and Utilizations of Cobalt. Chem. Age, vol. 19, No. 3, 1928, pp. 33-35. Min. Met. Sec.: Bureau of Mines Inf. Circ. 6331, August 1930, 33 pp.

"A newer process for separating Ni and Co is described briefly by Dyson. It involves the reactions of complex ammonia compounds. An ammoniacal solution containing cobalt chloride is oxidized by hydrogen peroxide (or merely by blowing air through it) so as to form what is known as rosecobalt chloride, the formula of which is $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_2$. This aquopentaminochloride when boiled is converted into chloropentaminochloride or chloropurpureocobalt, having the formula $[\text{Co}(\text{NH}_3)_5]\text{Cl}_2$."

834. EHREMAN, KURT, HAMPRECHT, GÜNTHER, SCHLECHT, LEO and TRAGESER, GEORG (assigned to I. G. Farbenindustrie, A. G.). [Separation of Cobalt and Copper.] German Patent 704,932, Mar. 13, 1941 (*Cl. 40a 43.30*); Chem. Abs., vol. 36, 1942, p. 1880^a.

Cobalt and Cu are readily separated by dissolving the Co with HCl or H_2SO_4 . The separation is sharp and complete if the S in the Co-Cu ore or alloy is present in sufficient amount to form insoluble sulfides of Cu.

835. ERSKINE, D. B. (assigned to Calumet & Hecla,

Inc.). Recovery of Nickel and Copper From Ammonium Carbonate Leach Solutions. U. S. Patent 2,638,220, Dec. 28, 1954; Chem. Abs., vol. 49, 1955, p. 4490e.

The preferential precipitation of Ni and Cu from ammonium carbonate leach solutions is accomplished by oxidation of 99 to 100 percent of the Cu in the solution to the cupric state, followed by vacuum distillation to remove enough NH_3 to precipitate Cu as the basic carbonate. In a variant procedure, NH_3 is distilled off approximately to the point of incipient precipitation, and CO_2 is bubbled through to precipitate the Ni, Pb, and Zn. After removal of the precipitate, further vacuum distillation of the filtrate precipitates pure Cu as the basic carbonate. The $\text{NH}_3:\text{CO}_2$ ratio must be kept low to avoid precipitation of Cu as oxide.

836. FALCK-MUUS, ROLF (assigned to Chemical Construction Corp.). Removal of Cobalt From Solutions Containing Nickel and Cobalt. U. S. Patent 2,690,391, Sept. 28, 1954; Chem. Abs., vol. 49, 1955, p. 824h.

In the recovery of high-purity Ni from ammoniacal ammonium salt solutions, the Co content is precipitated as a carbonate by adjusting the NH_3 and ammonium-salt content of the solution to retain Ni in solution and by heating the adjusted solution under pressure to more than 140°C . in the presence of hydrogen.

837. FORWARD, F. A. (assigned to Sherritt Gordon Mines, Ltd.). Recovery of Nickel and/or Cobalt Ammonium Sulfate From Solutions. U. S. Patent 2,647,820, Aug. 4, 1953 (see Chem. Abs., vol. 46, 1952, p. 1423c); Chem. Abs., vol. 47, 1953, p. 10,448b,d.

The ammoniacal solution is adjusted to approximately pH 7 by heating to remove excess NH_3 , which is recovered and reused, and then decreased to approximately pH 3 by addition of H_2SO_4 to precipitate Ni and/or cobalt ammonium sulfate at about 135°F . If the pH is adjusted to about 6.2 and O_2 is added to convert all Co to the cobaltic state, the major portion of the Ni is separated from the Co by precipitating as nickel ammonium sulfate. The metals may be recovered from the sulfates by roasting and reduction.

838. GUTMAN, M. I., AND MAYANTZ, A. D. [Freeing Nickel Sulfate Solutions From Iron and Aluminum Impurities.] Tsvetnye Metal, vol. 6, 1934, pp. 63-71; Chem. Abs., vol. 29, 1935, p. 4527⁵.

Solutions obtained by leaching the roasted mixture of Ni, Fe, and Al sulfates contained about 1 to 2 parts of Fe+Al to 1 part of Ni. A study was made of the optimum conditions for the precipitation of Fe and Al by means of MgCO_3 or CaCO_3 . Oxidation of Fe^{++} to Fe^{+++} was tried by means of MnO_2 , preliminary to treatment of the solution with carbonate or by means of aeration simultaneously with this treatment. The latter method, though slower, is to be preferred because introduction of additional Mn into the solution is avoided. The MgCO_3 , found in proximity to the Khalilovsk Ni-ore deposits, proved a suitable reagent for purifying the NiSO_4 solution.

839. ———. [Precipitation of Nickel Hydroxide in the Hydrometallurgical Treatment of Khalilovsk Nickel Ore.] Tsvetnye Metal, vol. 7, 1934, pp. 92-100 (see preceding abs.); Chem. Abs., vol. 29, 1935, p. 4527⁷.

Of the two methods, electrolytic and chemical, for separating Ni from the NiSO_4 solution in the treatment of Khalilovsk Ni ore, the first proved inapplicable. The chemical method consisted in precipitating the Ni as $\text{Ni}(\text{OH})_2$ from a solution containing 4.3 gm. Ni and 3.45 gm. Mn per liter by means of MgCO_3 or MgO . Results indicated that, at room temperature the reaction is very slow. In 5 hr. with agitation and 4 equivalents of MgCO_3 , 32-percent precipitation resulted; however, at boiling temperatures 1 equivalent of MgCO_3 caused 90-

percent precipitation in 5 hr. Magnesia proved more effective, for $1\frac{1}{2}$ equivalents at room temperature in 5 hr. gave nearly 100-percent precipitation and 1 equivalent gave 71-percent precipitation at room temperature in 5 hr., and 87 percent on boiling. Only small amounts of Mn precipitated. The precipitate obtained in these experiments contained 20 to 25 percent of Ni and is suitable smelting material.

840. HAMPRECHT, GÜNTHER, AND TRAGESOR, GEORG. [Separation of Nickel Salts From Solution.] German Patent 680,394, Aug. 10, 1939 (Cl. 12n 4) (see British Patent 498,152; Chem. Abs., vol. 33, 1939, p. 4387⁶); Chem. Abs., vol. 36, 1942, p. 2095⁸.

841. HILL, C. T. (assigned to The Pyrites Co., Ltd.). Separation of Cobalt From Solutions Containing Also Zinc and Nickel. U. S. Patent 2,232,527, Feb. 18, 1941; Chem. Abs., vol. 35, 1941, p. 3400³.

A warm solution containing Co, Zn, and Ni is treated with a soluble alkaline precipitant, such as Na_2CO_3 , until the pH rises to 7.0; Cl is then passed in until the pH falls to 2.5.

842. I. G. FARBENINDUSTRIE, A. G. [Separating Copper and Nickel.] French Patent 852,556, Feb. 27, 1940 (see U. S. Patent 2,180,520; Chem. Abs., vol. 34, 1940, p. 1607³); Chem. Abs., vol. 36, 1942, p. 2248⁷.

843. ———. [Separating Nickel From Other Heavy Metals.] French Patent 848,142, Oct. 24, 1939; Chem. Abs., vol. 35, 1941, p. 5450⁷.

A method of separating Ni from a hot solution containing Fe, Cu, and Ni consists in first converting the bivalent Fe to the trivalent state by oxidation and precipitating the Ni by means of concentrated HCl. The precipitation is made from hot solutions.

844. KOMATSUBARA, KYUJI. [Separation of Cobalt.] Japanese Patent 174,270, Dec. 10, 1946; Chem. Abs., vol. 44, 1950, p. 998f.

Nitrates of Ni and Co from ore are treated with a small quantity of acetic acid. After the addition of calcium carbonate in slight excess, the solution is boiled while simultaneously gassing with Cl_2 to precipitate the cobalt.

845. KOZU, T. [Separation of Aluminum From Manganese, Nickel, Cobalt, and Zinc.] Jour. Chem. Soc., Japan, vol. 56, 1935, pp. 683-688 (see British Chem. Abs., 1935, p. A-1338); British Chem. Abs., 1936, p. A-813.

Aluminum is precipitated quantitatively from sulfate solution at room temperature by adding saturated aqueous NH_4Ph . Zinc interferes, but K, Mn, Ni, and Co do not.

846. KURT, ALBERT, G. M. B. H. CHEMISCHE FABRIKEN. Separation of Copper and Nickel. British Patent 458,959, Dec. 30, 1936 (see French Patent 799,907; Chem. Abs., vol. 30, 1936, p. 8138³); Chem. Abs., vol. 31, 1937, p. 3860².

847. ———. Separation of Copper and Nickel. British Patent 467,517, June 18, 1937 (see French Patent 799,907; Chem. Abs., vol. 30, 1936, p. 8138³); Chem. Abs., vol. 31, 1937, p. 8493⁸.

848. ———. [Copper and Nickel.] French Patent 799,907, June 23, 1936; Chem. Abs., vol. 30, 1936, p. 8138⁴.

Cu is precipitated from solutions containing Cu compounds by Ni metal above 100°C . and under increased pressure. Alloys or waste materials containing Cu and a greater proportion of Ni are solubilized with acids above 100°C . under increased pressure, whereby the Ni forms a salt with the acid and the Cu is precipitated.

849. LICHTENWALTER, MYRL (assigned to Nicaro Nickel Co.). Separation of Copper From Nickel in Am-

moniacal Solutions. U. S. Patent 2,440,612, Apr. 27, 1948; Chem. Abs., vol. 42, 1948, p. 5405b.

Cu solutions obtained by leaching operations are reduced to the cuprous state by the action of metallic Cu, and Cu is precipitated as copper acetylide by passing C_2H_2 through the solution. The separation is quantitative, but Cu carries with it all the Au and Ag. Copper acetylide is decomposed with H_2SO_4 , C_2H_2 recovered, and $CuSO_4$ electrolyzed.

850. MAKISHIMA, GENICHIRO (assigned to Chuetsu Electrochemical Industries Co.). [Refining of Nickel Salt Solution Containing Cobalt Salt.] Japanese Patent 2607, June 10, 1953; Chem. Abs., vol. 48, 1954, p. 7858h.

A solution (1 l.) containing 50 gm. of $NiCl_2$ and 1.5 gm. of $CoCl_2$ is used, 100 gm. of which is treated with 10 gm. of $CaCO_3$. Cl gas is passed in for 5 minutes at $25^\circ C.$, at the rate of 10 ml./min., to precipitate the cobalt. The filtered, washed precipitate contains 0.017 percent Ni, and the Ni filtrate contains only a trace of Co.

851. MCGAULEY, P. J. (assigned to Chemical Construction Co.). Isolation of Nickel Sulfide. U. S. Patent 2,588,265, Mar. 4, 1952; Chem. Abs., vol. 46, 1952, p. 5797e.

Ore containing Ni and other nonferrous metals is subjected to an oxidizing leach, the oxidized slurry removed from the system and filtered off, and the filtrate divided into 2 portions; 1 of them is neutralized with NH_3 to pH 4.0 to 6.8 and Ni precipitated as nickel ammonium sulfate. The other is treated with a soluble reducing agent in combination with an ore concentrate, having Fe and S content equivalent to the non ferrous metal content in the filtrate, at 275° – $750^\circ F.$ This precipitates sulfides of the nonferrous metals, which are separated from the filtrate and returned to the leaching operation.

852. — (assigned to Chemical Construction Co.). Recovery of Nickel From Ammoniacal Liquors. U. S. Patent 2,647,828, Aug. 4, 1953; Chem. Abs., vol. 47, 1953, p. 10,447i.

Nickel ore containing Cu, Fe, and/or Co is given an acid or ammoniacal leach and filtered to remove undissolved solids. The filtrate is adjusted to a pH of 3 to 4 to remove Fe; adjusted to an $(NH_4)_2SO_4$ concentration of 10 to 40 percent; adjusted to a Cu content varying from 8 percent maximum, at 10 percent $(NH_4)_2SO_4$ concentration, to a 1-percent maximum, at 40 percent $(NH_4)_2SO_4$ concentration; adjusted to a Co content of 5 percent at 10 percent $(NH_4)_2SO_4$ to 1.5 percent maximum at 40 percent $(NH_4)_2SO_4$; and the pH is adjusted to 4 to 6.5 to precipitate a complex nickel double salt from which Ni may be readily obtained. Operating temperatures are 25° – $325^\circ C.$

853. MOND NICKEL CO., LTD. Purification of Cobaltic Hydroxide. British Patent 575,259, Sept. 29, 1943; Canadian Patent Oct. 16, 1942; British Abs., 1946, p. B-I-168.

Cobaltic hydroxide contaminated with Ni, Fe, Cu, As, and Pb is made into a slurry with water. Upon reduction, as, for example, with SO_2 , and treatment with H_2SO_4 to pH 4.5 to 1, preferably to pH 2.0, Ni, Co, Cu, and at least some Fe are dissolved. The solution, separated from insoluble matter, is then treated with further impure $Co(OH)_3$, which oxidizes reduced Fe and Cu, Fe being precipitated and acting as collector for As and Pb. The resultant solution, containing Co, Ni, and Cu, is purified further by removal of Cu by cementation. Cobalt is finally separated from Ni, in known manner, by precipitation, and if necessary, reprecipitation as $Co(OH)_3$, by addition of $NaOCl$.

854. MOND NICKEL CO., LTD., WALLIS, A. E., AND WEST, DE, W. H. Production and Purification of Cobaltic

Hydroxide. British Patents 570,230, Nov. 28, 1941, and 570, 231, Sept. 4, 1942; British Abs., 1945, p. B-I-329.

(A) Cobaltic hydroxide containing only small amounts of Ni is precipitated from Ni-containing Co solutions by addition of $Ni_2(OH)_4$ at 40° – $60^\circ C.$ and adjusting the pH to 1 to 2.4, preferably 1.8.

(B) Nickel is largely removed from $Co_2(OH)_4$ by digestion at $70^\circ C.$ in an acid liquor, pH 0.9 to 2, containing a Co salt; the presence of the Co salt can be insured by adding a reducing agent, for example, SO_2 or Na_2SO_3 , to the acid.

855. MUKOYAMA, MIKIO, AND ANDO, TOKUICHI (assigned to the Minister of Commerce and Industry). [Separation of Nickel From Manganese.] Japanese Patent 176,808, Oct. 15, 1948; Chem. Abs., vol. 45, 1951, p. 4898h.

To a part of a solution containing Ni and Mn, alkali or alkali carbonate is added in the form of an oxide or hydroxide. Further addition of alkali and heating in an autoclave with oxygen at 200° – $400^\circ C.$ converts the Mn to MnO_4^- , which is separated by filtration from the Ni precipitate. The MnO_4^- is added to the remaining solution, and Mn is precipitated as manganese oxide at pH 2 to 6.

856. NAKAO, TOMOSBORO (assigned to Sumitomo Electrochemical Industries Co.). [Recovery of Cobalt Oxide From Impure Cobalt.] Japanese Patent 6,875, Oct. 30, 1951 (see Chem. Abs., vol. 46, 1952, p. 11,609c); Chem. Abs., vol. 47, 1953, p. 3784h.

An impure Co is dissolved in HNO_3 and filtered, ammonium hydroxide is added up to pH 5 to 6 to precipitate hydrated ferric oxide and aluminum oxide, the filtrate is treated with NH_4OH to pH 7 to 8.5, to precipitate cobaltous hydroxide, and filtered. The hydroxide is ignited to cobaltic oxide.

857. PERELMAN, F. M. [Separation of Cobalt and Nickel Chlorides.] Russian Patent 51,372, July 31, 1937; Chem. Abs., vol. 33, 1939, p. 7055⁴.

Cobaltous chloride and $NiCl_2$ are separated by crystallization in the presence of KCl .

858. PLETENEV, S. A. [Development of Process for Extraction of Cobalt From Domestic [Russia] Raw Materials.] Tsvetnye Metal, No. 8, 1939, pp. 69–81. Chem. Abs., vol. 34, 1940, p. 4708⁴.

In this process the Co impurity precipitated with $Ni(OH)_2$ is treated to recover the Co. The cake, dissolved in H_2SO_4 , is oxidized with $NaClO$ and precipitated with $NaOH$ in a 3-hour operation, increasing the Co content; this operation is twice repeated, dissolving in H_2SO_4 and precipitating as before. The final product contains all of the Co and analyzes less than 2 percent Ni; this process is also applied to a byproduct cake from $NiSO_4$ manufacture and to slags.

859. RENZONI, L. S. (assigned to International Nickel Co.). Purification of Cobalt Precipitates Containing Iron and Other Impurities. U. S. Patent 2,367,239, Jan. 16, 1945; Chem. Abs., vol. 39, 1945, p. 3239⁷.

A solution containing Ni, Co, Cu, Fe, As, and Pb in the reduced state is treated with O_2 or O_2 -containing gas, chlorine, and enough alkali to precipitate the iron salts. The other metals will also precipitate. Now enough SO_2 is introduced to reduce Co, Ni, and a part of the Fe. H_2SO_4 and an oxidizing agent, preferably the first precipitate, are now introduced to provide a pH of about 4.5 and oxidize the Fe, which hydrolyzes to precipitate Fe, Pb, and As. The precipitate is removed. The solution, containing Ni, Co, and Cu, is treated with Ni powder to cement out the Cu and sodium hypochlorite, to separate Co from the solution. The solution is recycled to the first step. The Co precipitate, solubilized with SO_2 and H_2SO_4 , is again precipitated with sodium hypochlorite to remove 2 to 4 percent Ni content. The washed Co precipitate is roasted

at 2,100° F., again leached with water to remove soluble salts, and finally dried to assay about Co 70 and Ni 0.8 percent.

860. RODER, OSCAR. [Cobalt Oxidation.] German Patent 643,814, Apr. 17, 1937 (*Cl. 12n 4*); Chem. Abs., vol. 31, 1937, p. 5960⁶.

A method of oxidizing Co to form higher oxides or to separate Co from other metals consists of treating Co or cobalt compounds with chlorate solution at temperatures above 100° C. and under raised pressure. The chlorate solution may be neutral or weakly acid or alkaline. Thus, CoSO₄ solution is treated with NaClO₃ solution to give a precipitate of Co₂O₃. Also, a mixture of CoSO₄ and NiSO₄ is treated with NaOH and NaClO₃. Nearly all the Co is precipitated as Co₂O₃, the Ni remaining in solution.

861. ROELEN, OTTO, AND SCHALLER, PAUL (assigned to Ruhrchemie A. G.). [Purifying Cobalt Solutions.] German Patent 683,691, Oct. 26, 1939 (*Cl. 12n 4*); Chem. Abs., vol. 36, 1942, p. 4297⁶.

Ca is removed from Co solutions by precipitating it with fluorine, in the presence of Mg. If any Fe or Al is present, the solution pH is adjusted to 6 to 7, and the Fe and Al are precipitated with an alkali carbonate. The pH of the filtrate is reduced to 2 to 4 and the Ca precipitated with NaF in the presence of Mg. This method is applicable for regenerating Co catalysts. Any Mg remaining will not adversely affect the catalyst.

862. SAMUEL, J. O. (assigned to Unifloc Reagents, Ltd.). Removing Iron Impurities From Nickel and Cobalt Solutions. British Patent 516,657, Jan. 8, 1940; Chem. Abs., vol. 35, 1941, p. 6230⁶.

Fe impurities are removed by precipitating ferric hydroxide and adding to the hot solution (70°–100° C.) a proportion of an aqueous pulp of a cellulose material with nickel or cobalt peroxide or higher oxide, which, in the presence of O₂, oxidizes the precipitated iron, and filtering.

863. SCHAAL, R. B. (assigned to Ferro Enamel Corp.). Separation of Nickel From Cobalt. U. S. Patent 2,488,561, Nov. 22, 1949; Chem. Abs., vol. 44, 1950, 1392d.

An aqueous solution of nickel and cobalt chlorides is treated with gaseous Cl₂ in the presence of CaCO₃ in quantities sufficient to counterbalance all HCl produced. This precipitates all Ni and Co as hydroxides. Chlorination is continued until most of the more soluble Ni(OH)₂ is dissolved, after which Co(OH)₂ is filtered off. Ni is precipitated from chlorides with CaCO₃ or alkalis.

864. SCHAUFELBERGER, F. A. (assigned to Chemical Construction Co.). Separation of Nickel and Cobalt Metal From Acidic Solution. U. S. Patent 2,694,005, Nov. 9, 1954; Chem. Abs., vol. 49, No. 4, 1955, p. 2287g, h, i.

High-purity Ni is separated hydrometallurgically from acidic solutions containing Co and Ni and substantially Cu- and Fe-free. The pH is adjusted to acidic conditions with a free acid content of approximately 5 percent, and the solution is heated to above 250° F. in the presence of a nonsulfidizing reducing gas and a compatible electrolyte, whereby the anion of the electrolyte forms a gas-reducible anion complex with the Ni-ion and the Ni is reduced to metal. The reduction is continued in the presence of a soluble-salt-forming, acid-neutralizing agent, which, after reduction, produces a H-ion concentration of 0.1 to 0.2 percent for original Ni:Co molecular ratios of 5:1 and concentrations up to 1 percent for Ni:Co ratios of 1:1 to 1:10. When the Ni precipitation ceases, the precipitate is removed, and a solution suitable for Co metal precipitation is obtained. A solution is prepared by

dissolving in 0.2 part aqueous H₂SO₄, approximately 0.5 part (NH₄)₂SO₄, and 0.75 part of a cobalt sulfate mixture having a Ni:Co ratio of 1:1. The solution is transferred to a stirred autoclave and heated to 400° F. with the pressure raised to 800 p. s. i. with H₂. Enough NH₃ is added to produce 0.5 percent free acid after reduction. After 30 min., the treatment is stopped, the pressure is relieved, and the solids are collected. The filtrate is re-treated under similar temperature and pressure after neutralization of the free acid with added NH₃. In the first product, the Ni powder contains approximately 2.5 percent Co, and the second contains approximately 97 percent of the original Co with 2.3 percent Ni.

Purer materials are obtained by carrying the reductions to a lower cutoff acidity of 0.2 percent free acid.

865. — (assigned to Chemical Construction Co.). Precipitation of Cobalt From Cobalt-Nickel Salt Solutions. U. S. Patent 2,711,950, June 28, 1955; Chem. Abs., vol. 49, 1955, p. 12,260h.

Solutions containing nickel and cobalt carbonates and sulfates are treated with NH₃ and CO₂ and heated. Cobalt is precipitated as the carbonate, effecting a separation of the two metals. Thus, a solution containing 21.5 gm. per l. of Co and 28 gm. per l. of Ni as sulfates was adjusted to contain 50 gm. per l. of free NH₃ and 280 gm. per l. of (NH₄)₂CO₃. After heating at 160° C. for 20 minutes, the precipitate contained 99.4 percent of the Co and less than 0.02 percent of the Ni. The filtrate contained 22.4 gm. per l. of Ni and 0.1 gm. per l. of Co. Metallic Ni can be readily precipitated from the filtrate. The Co concentrate contained less than 5 percent of Ni. (See following two abs.)

866. SCHAUFELBERGER, F. A., AND MCGAULEY, P. J. (assigned to Chemical Construction Co.). Separation of Nickel and Cobalt From Amine Solution. U. S. Patent 2,694,006, Nov. 9, 1954; Chem. Abs., vol. 49, 1955, No. 4, p. 2288a.

Substantially Ni-free Co is separated from a mixture containing both metals by preparing an aqueous solution containing dissolved Co and Ni at 275°–400° F. and then treating with a nonsulfidizing reducing gas and a complex-forming amine to produce a solution of mol. ratio of unneutralized amine to dissolved Co plus Ni of approximately 1.5:4. The Ni metal powder is precipitated and removed. Ammonia is added to the residual solution to produce an amine : dissolved-Co ratio above 4. Cobalt is precipitated by further reduction at a higher temperature and is collected. One part of a crystal mixture of cobalt and nickel sulfides having a Ni : Co ratio of 4 : 5, which had been previously treated to recover Cu, is dissolved in H₂O, with 1.2 parts of (NH₄)₂SO₄. The acidity of the solution is about pH 4.5. The slurry is transferred to a stirred autoclave and treated with 100 gm./l. of Ni powder, 2 moles of NH₃ per mole of metal, and enough H₂ to maintain a pressure of 800 lb. p. s. i. at 350° F. Treatment at 320°–400° F. is conducted for ½ hr. Up to 40 percent of the Ni is precipitated as metal powder containing less than 2 percent Co. In a second treatment, by using up to 0.5 additional part of NH₃, most of the remaining Ni is coprecipitated with Co at 350°–425° F. In a third treatment above 400° F., approximately 40 to 50 percent of the Co is recovered in a fraction containing 3 to 6 percent Ni. Substituted amines, such as ethylamine or ethylenediamine, can be used in place of NH₃.

867. SCHAUFELBERGER, F. A., AND ROY, T. K. (assigned to Chemical Construction Corp., New York). Nickel-Cobalt Separation by Selective Reduction. Prepr. of paper to be presented at annual meeting AIME, Chicago, Feb. 14–17, 1955.

"Abstract: After reviewing various methods for Ni-Co separation, a novel technique of stepwise precipitation of Ni and Co, with reduction by H_2 gas, is described. In using this technique, reduction to elemental powder is obtained concurrently with separation of Ni from Co into products of commercially acceptable metal purity. Data from batch and continuous operation are presented."

868. SHELTON, F. K. (assigned to the United States of America, as represented by the Secretary of the Interior). Separation of Nickel and Cobalt. U. S. Patent 2,508,427, May 23, 1950; Chem. Abs., vol. 44, 1950, p. 7743d.

Co and Ni, mixed in the form of their carbonates, may be separated by reducing to -65-mesh, leaching out the water-soluble salts, heating either steadily or intermittently at about 200° C. for about 7 to 10 days to calcine the mixture, and then leaching this product with a dilute mineral acid, the pH being kept at about 2.0. The solid residues contain about 75 percent of the original Co in Co : Ni ratio about 10 times that of the original.

869. SOCIÉTÉ GÉNÉRALE MÉTALLURGIQUE DE HOBOKEN. Separation of Nickel and Cobalt From Their Alloys. British Patent 655,149, July 1, 1949, amended (see British Abs., 1951, p. B-1-1259); British Abs., 1952, p. B-1-1146.

The primary material, containing Co and Ni, is treated with a dilute acid (H_2SO_4 or HCl) in the presence of S, Se, As, Te, Sb, or their compounds, the solution being maintained at pH 1.5 to 5.5, so as to fix the Ni as an insoluble compound while the Co passes into solution. The treatment is carried out preferably in presence of Fe and of a solution containing Co and Ni, the Ni of the solution being precipitated with the Ni of the original material.

870. SÜTTERLIN, WALTER (assigned to I. G. Farbenindustrie, A. G.). [Separating Heavy Metals, Such as Zinc, Cadmium, and Nickel, From Solutions Containing Iron and Sulfates.] German Patent 720,881, Apr. 16, 1942 (Cl. 12n 1); Chem. Abs., vol. 37, 1943, p. 2330².

To the leach solution is added lime or $CaCO_3$ and a H_2S -containing gas (for example, generator gas) is passed through the hot solution to a pH of approximately 2. The precipitate is suspended in water, and the heavy metal sulfides are separated in the usual way with the aid of flotation agents.

871. UNIFLOC REAGENTS, LTD., AND SAMUEL, J. O. Manufacture of Nickel and Cobalt Salts. British Patent 516,657, July 5, 1938; British Chem. Abs., 1940, p. B-526.

A Ni or Co solution to which a carbonate has been added to effect removal of Fe is treated at 70°-100° C. with wood or paper pulp and NiO_2 or Co_2O_3 (8 to 20 lb. per 100 gal.) and then filtered.

872. WALLIS, A. E., AND PINCOTT, JOHN (assigned to Mond Nickel Co., Ltd.). Cobaltic Hydroxide. British Patent 707,741, May 12, 1954 (see Chem. Abs., vol. 40, 1946, p. 5214¹); Chem. Abs., vol. 48, 1954, p. 14,138e.

In the process for preparing $Co(OH)_3$, greater purity can be attained by effecting the precipitation at a temperature below 12° C. instead of in the range of 40°-60° C. Separation from the Ni impurity is enhanced at the lower temperature because the Co : Ni ratio in the precipitate becomes higher as the temperature is reduced.

873. WALLIS, A. E., AND WEST, DE W. H. (assigned to International Nickel Co.). Precipitation of $Co(OH)_3$. U. S. Patent 2,377,832, June 5, 1945 (see Application Ser. No. 472,874); Chem. Abs., vol. 39, 1945, p. 3637².

Hydrated nickel oxide is added to an aqueous solution containing soluble cobalt salts to precipitate $Co(OH)_3$, the aqueous solution being maintained at pH 1.0 to 2.4 and a temperature of 40°-60° C.

874. — (assigned to International Nickel Co.). Removal of Nickel From Cobaltic Hydroxide Precipitates. U. S. Patent 2,415,665, Feb. 11, 1947 (see Chem. Abs., vol. 39, 1945, p. 3637²); Chem. Abs., vol. 41, 1947, p. 2542e.

In recovery of Co from its complex ores, an intermediate product of $Co(OH)_3$ is obtained, which generally requires purification from Ni. The present patent proposes to effect this purification by a process of base exchange, involving the digestion of the precipitate by Co solutions at controlled pH. A preferred procedure is to treat the precipitate in a H_2SO_4 solution of 1.5 to 2.0 pH at 70° C. Part of the Co is leached out and undergoes base exchange, so that the remaining $Co(OH)_3$ contains less Ni. A further purification can be made by a second leach with pure $Co_2(SO_4)_3$ solution. Crude precipitates containing Co : Ni ratios as low as 4 : 1 can be purified by this process to contain less than 1 percent of Ni.

875. WESLEY, W. A. Oxidizing Agents for Nickel Solutions. Metal Ind., N. Y., vol. 33, 1935, p. 290 (see British Chem. Abs., 1935, pp. A-45 and A-1467); British Chem. Abs., 1936, p. A-948.

876. WILLE, ALBERT, AND VÖLKE, WALTER (assigned to Deutsche Gold- u. Silber-Scheideanstalt vormals Roessler.). [Removing Iron From Solutions of Nickel and Cobalt.] German Patent 628,514, Apr. 6, 1936 (Cl. 48a 6.05); Chem. Abs., vol. 30, 1936, p. 5929³.

Fe is removed from Co and Ni solutions by addition of a small amount of alkali perphosphate (for example, 5 to 8 gm. of ammonium perphosphate per liter). The Fe is precipitated and the solution rendered suitable for use.

HYDROWINNING OXIDIZED ORES LEACHING

877. BOGATSKII, D. P. [Basis of New Combined Methods of Treating Oxidized Nickel-Cobalt Ores, Using Waste Sulfur Dioxide.] Bull. Acad. Sci., U. R. S. S. (Cl. Sci. Chem.), 1944, pp. 272-282; British Abs., 1945, p. B-1-302.

Ores from the Aidarbakh-Khalilov strata, or tailings from the flotation process are tested. After reduction, leaching with either H_2SO_4 or with acid and recovered SO_2 extracts 99 percent of the Ni and most of the Co, effecting a saving in cost and in time over conventional methods. The expenditure of H_2SO_4 is 30 to 40 tons per ton of Ni, even for the most difficult silicate-oxidized Ni waste ores; the SO_2 is derived from the waste gases from H_2SO_4 manufacture.

878. BOGATSKII, D. P., AND SEMENOVA, A. S. [Ammoniacal Treatment of Lateritic Nickel Ores.] Jour. Applied Chem., U. S. S. R., vol. 20, 1947, pp. 89-96 (in Russian); Chem. Abs., vol. 41, 1947, p. 7338d.

Leaching was done with an aqueous solution of $(NH_4)_2CO_3$ with an excess of NH_3 (up to 13 percent in NH_4OH , 12 percent in CO_2).

Ores leached were (1) a nickel oxide prepared by heating $Ni(NO_3)_2$ at 1,100° C., (2) nepouite-garnierite, (3) nickel aluminosilicate, and (4) and (5) 2 nickel silicate ores containing Fe and Al. Upon grinding to minus-200-mesh and direct leaching, none of the materials yielded a significant amount of Ni; hence, all materials were first reduced in H_2 under the in-

dividual optimum conditions, between 700° and 1,000° C. for 3 hr. The leaching process requires a temperature of 40°–45° C.; higher temperature entails a loss of NH_3 . The leaching yields of Ni are given for the various reduced ores and for increasing the duration of leaching; yields vary from 70 percent in 5 hr. to more than 90 percent in 26 hr. Ammoniacal leaching is less effective than chlorination or H_2SO_4 extraction.

879. CARON, M. H. [Extracting Nickel and Cobalt From Ores.] *Netherland Patent* 43,343, June 15, 1938; *Chem. Abs.*, vol. 33, 1939, p. 2867⁴.

Recovering Co or Ni from reduced ores by neutral or ammoniacal ammonium salt solution (Netherland Patent 12,975) is often hindered by gas adsorption in the finely divided metal. The extraction of such metal is possible by adding KCN, KCNS, or other CN derivative (approximately 0.01 percent) to the cold, weak, extraction solution.

880. DE OLIVEIRA, EUZEBIO. [Metallurgy of Nickel: A New Use for Native Coal.] *Ann. acad. brasil. sci.*, vol. 3, 1931, pp. 75–77; *Chem. Abs.*, vol. 26, 1932, p. 1223.

In Brazil Ni occurs as garnierite. The fusion of garnierite by heating with coke is too expensive for practical purposes. A method has been developed whereby coal from southern Brazil, high in pyrites, is subjected to heat and moisture; this causes a breaking down to give an acid liquor, which in the coal will dissolve garnierite much more readily than H_2SO_4 of the same concentration. The pyrites of this coal is marcasite. Common pyrites, unlike marcasite, when subjected to heat and moisture, gives free S and Fe oxide and this with much difficulty. Ores with as low as 2.5 percent Ni can be successfully treated.

881. DOLIVO-DOBROVOLSKII, V. V. [Problem of Concentration of Low-Grade Nickel Ores.] *Gorno-Obogatitelnoe Delo*, No. 2–3, 1932, pp. 59–68; *Chem. Abs.*, vol. 27, 1933, p. 3174.

Samples of Khalilov, Tyulenev, and Malksk Ni-Fe ores containing 0.40–1.34 Ni, 22.64–63.10 Fe_2O_3 , and 0.36–0.87 percent Cr were treated with 2-, 5-, and 10-percent solutions of H_2SO_4 for periods varying between 1 and 48 hr., also with 5-percent oxalic acid for periods of 3 to 24 hr. Maximum extraction of Ni (up to 94.4 percent) and of Fe (up to 84.9 percent) was obtained by treating Khalilov ore with 10-percent H_2SO_4 for 12 hr.

882. DU FAUR, B. Hydrometallurgical Treatment of Cobalt Ores. *Chem. Eng. and Min. Rev.*, vol. 35, 1942, pp. 14–19; *Eng. Index*, 1944, p. 218; *Chem. Abs.*, vol. 37, 1943, p. 587⁴.

A method of recovering Co from its ores comprises steps for (1) solubilizing Co as sulfate, (2) removal suitable treatment, and in the third step cobalt carbonate. In the first step, a 5-percent excess of sulfuric acid over the theoretical stoichiometrical amount for all metals was mixed with ore, and a small source of heat was applied until water had been removed and a solid mass resulted. The broken-up mass dissolved in water was freed of iron by pH adjustments and air oxidation in the second step. Copper was removed by suitable treatment, and in the third step cobalt carbonate was precipitated by addition of sodium carbonate.

883. ———. Hydrometallurgical Treatment of Cobalt Ores. *Chem. Age*, vol. 51, No. 1323, Nov. 4, 1944, (Met. Sec.), pp. 443–444; *Eng. Index*, 1944, p. 218.

Extracts from paper indexed in *Eng. Index*, 1942, p. 234, from *Chem. Eng. and Min. Rev.*, Oct. 10, 1942.

884. GEE, E. A., AND HUFF, W. J. Incremental Digestion. *Chem. Eng. Progress*, vol. 50, No. 6, June 1954, pp. 299–304; *Eng. Index*, 1954, p. 757.

By digesting silicate ores through incremental stages

of HCl treatment, their filtration rates were increased 10-fold, indicating possible wide application among certain marginal and submarginal ores of silicic composition. The applicability of the method to olivine ore, an important potential source of magnesium, chromium, and nickel, and to other ores is discussed (6 refs.).

885. GIROTTI, ALEXANDRE. [The Utilization of Coals From Southern Brazil.] *Ann. acad. brasil. sci.*, vol. 3, 1931, pp. 79–81; *Chem. Abs.*, vol. 26, 1932, p. 1223.

The action of the acid liquor from the marcasite-containing coals on garnierite was studied. The acid liquor has more than twice the dissolving power of H_2SO_4 . A solution of H_2SO_4 , FeSO_4 , and $\text{Fe}_2(\text{SO}_4)_3$, to approximate the composition of the liquors obtained from the coal, is inferior in dissolving power. Ammonia as a catalyst was considered, but the amount found in acid liquor is very minute and thought to be probably due to a slight decomposition of volatile matter in the coal. The effect of biological agents from the coal or surrounding atmosphere relative to the action of these acid liquors is being investigated. Conditions of temperature and concentration suitable for industrial application are being studied.

886. GUIMARAES, CYRO, AND MOLIAN, T. R. M. [The Decomposition of Some Complex Silicates of Nickel by Certain Mineral Acids.] *Inst. pesquisas technol.*, São Paulo, Anais, Assoc. quim. Brasil, vol. 9, 1950, pp. 75–87; *Chem. Abs.*, vol. 46, 1952, p. 390a.

In studying various economic processes for extracting Ni from its ores, it was found that the nickel silicates are not decomposed quantitatively by HNO_3 , HCl, or HClO_4 . Satisfactory results are obtained with H_2SO_4 . The proportion of acid to silicate is 0.92 gm. of acid to 1 gm. of mineral.

887. HAYWARD, C. R. (assigned to Bethlehem Steel Corp.). Treatment of Iron Ore Containing Impurities, Including Nickel and Chromium. U. S. Patent 2,584,700, Feb. 5, 1952; *Chem. Abs.*, vol. 46, 1952, p. 3939i.

Cr, Al, Si, Ni, and Co are removed from Mayari (Cuba)-type ores containing a minimum of 0.5 percent Cr and 0.25 percent Ni. The ore is leached in 5 N H_2SO_4 ; Cr and Si separate out. The acidity is then reduced by the addition of ore and sponge Fe. Ni, Co, Cr, and Al are precipitated and filtered. The filtrate, consisting of ferrous sulfate and H_2SO_4 , is evaporated, and the resulting crystals are calcined at 1,100° F. to form refined Fe ore.

888. HEDLEY, NORMAN, AND KRESS, J. J. (assigned to American Cyanamid Co.). Treatment of Garnierite Ores. U. S. Patent 2,349,223, May 16, 1944; *Chem. Abs.*, vol. 39, 1945, p. 689³.

The ore is ground, roasted, and then leached with a 3:1 solution of SO_2 preferably in two steps. The first leach extracts approximately 80 percent of Ni present. The slurry may be filtered or the solids separated by settling. The latter are subjected to another leaching with a fresh SO_2 solution, and approximately 5 to 6 percent more Ni is recovered. In addition, the leach solution contains Cu, Co, and Fe as sulfites, thiosulfates, and the like. The excess SO_2 is removed by boiling, and Cu may be precipitated as CuS . To the filtrate is gradually added Na₂S to precipitate the remaining Ni without precipitating Fe. The precipitate is granular and settles and filters readily. It may be calcined to give a crude oxide containing 60 to 70 percent Ni, and the SO_2 given off may be utilized in the leaching step.

889. HILLS, R. C. (assigned to Nicaro Nickel Co.). Recovery of Nickel and Ammonia. U. S. Patent 2,400,114, May 14, 1946; *Chem. Abs.*, vol. 40, 1946, p. 4338⁴.

A finely divided, reduced nickel oxide ore is leached in several stages with a solution containing 3 percent

NH₃ as carbonate and 3 percent NH₃ as hydroxide, accompanied by aeration. Substantially all of the Ni is rendered soluble. The Ni-bearing solution, contained in the tailings, is then removed by washing with fresh leaching solution instead of washing by water, as heretofore. Water washing would precipitate the dissolved Ni on the ore particles. The tailings pulp, containing an appreciable amount of the NH₃ solution, is treated in a still with steam to recover the NH₃.

890. HILLS, R. C., AND DUFOUR, M. F. (assigned to Nicaro Nickel Co.). Recovery of Nickel and Cobalt Compounds. U. S. Patent 2,531,336, Nov. 21, 1950; Chem. Abs., vol. 45, 1951, p. 1739b.

In recovering the Ni and Co from ammoniacal leach liquors, a small content of S, Se, or Te tended to prevent oxidation of Co and interfered with the process in which the NH₃ was distilled off until nickel carbonates precipitated, and after Ni removal, further distillation precipitated Co salts. In this patent, an alkali metal carbonate is first added and the solution aerated to remove S, Se, and Te before the distillation process. An alternative method of removing these impurities is severe oxidizing treatment of the leach liquors, as with hydrogen peroxide or electrolytic oxidation.

891. HUBLER, W. G., AND ARCHIBALD, F. R. (assigned to Ventures, Ltd.). Treating Lateritic Ores. U. S. Patent 2,105,456, Jan. 11, 1938; Chem. Abs., vol. 32, 1938, p. 2302².

Hydrous silicate ores containing Fe, Ni, and Mn, such as garnierite or noumeite, are crushed and leached with a cold dilute solution of HCl. Fe and Ni are selectively removed from the resulting solution by successive precipitations with magnesia. HCl and magnesia are recovered from the remaining solution.

892. KAWAMURA, KYOJI. [Extraction of Nickel From Ore.] Japanese Patent 172,870, June 10, 1946; Chem. Abs., vol. 46, 1952, p. 1423e.

Nepouite is extracted with H₂SO₄, HCl, or HNO₃, saturated with an Fe salt. Nickel is precipitated from the hot solution as basic chromate or oxalate. This method saves the amount of acid required to dissolve Fe contained in the ore.

893. MÜLLER, R. M., HESSE, WALTER, AND SINIGOI, FRANZ. [The Dressing of Serpentine and Their Weathering Products by Leaching With Acid.] Berg.-u. hüttenmänn. Monatsh. montan. Hochschule Leoben, vol. 96, 1951, pp. 209-214; Chem. Abs., vol. 46, 1952, p. 1937a.

A method was developed that makes it possible to produce Ni profitably, even from ores with very low Ni content (0.3 percent). The serpentines are treated with steam containing about 20 percent HCl at 50° to 200° C., whereby MgO, FeO, Al₂O₃, and Ni are dissolved and a white solid SiO₂ skeleton remains.

894. OGANESYAN, M. A. [Treatment of Serpentine.] Russian Patent 52,891, Mar. 31, 1938; Chem. Abs., vol. 34, 1940, p. 5606².

Serpentine is heated with a solution containing NH₄Cl, in particular with that obtained as a byproduct in the Solvay soda process. The liberated NH₃ is recovered, Ni and Mg compounds are obtained from the solution, and the residue is converted into active SiO₂ by known methods.

895. PAWEL, G. W. (Norris, Tenn.). Acid Leaching Oxidized Ores Offers New Source of Nickel. Eng. and Min. Jour., vol. 153, No. 10, 1952, pp. 94-95; Chem. Abs., vol. 47, 1953, p. 12,165i; Metals Rev., vol. 25, No. 11, November 1952, p. 24 (150-e).

Leaching an oxidized ore containing 2 to 5 percent of Ni with strong HCl vapors dissolves 90 percent of the Ni and 60 percent of the magnesia. Ni and Fe are precipitated from the chloride liquors by adding mag-

nesia. The precipitate is subsequently reduced to ferro-nickel. Magnesia and HCl are recovered by evaporation and decomposition of the filtrate.

896. TATEBE, TOSHIO. [Research on the Ammonia Leaching Process of Garnierite Ore.] Proc. World Eng. Congr., Tokyo, 1929, vol. 35, 1931, pp. 217-235; Chem. Abs., vol. 25, 1931, p. 5371⁴.

Garnierite ore, after pulverization, is reduced with CO and H₂ at 800°-850° C. and cooled to prevent re-oxidation. The product is leached countercurrently with NH₄OH and (NH₄)₂CO₃ in the presence of O₂ or air. Metallic Ni is dissolved as NiCo₃.nNH₃, where n is probably 3. After filtration the filtrate is heated. NH₃ and CO₂ are distilled, and basic carbonate of Ni is deposited. This was calcined to NiO and reduced to Ni by the ordinary processes.

PRECIPITATION AND SEPARATION

897. FITZHUGH, R. R., FREDERICK, B. F., AND AXELRAD, B. A. (assigned to Nicaro Nickel Co.). Ammonia Recovery From Ore-Tailings Pulp. U. S. Patent 2,458,902, Jan. 11, 1949; Chem. Abs., vol. 43, 1949, p. 2919h.

The Mg impurities in the nickeliferous ore-tailings pulp are precipitated by heating to 150° F., and the ammonia is then distilled from the pulp in a distillation column.

HYDROWINNING NONOXIDIZED ORES LEACHING

898. BACON, R. F., AND BENCOWITZ, ISAAC. Treating Ore Containing Pyrites and Sulfides of Copper and Nickel. U. S. Patent 1,917,235, July 11, 1933; Chem. Abs., vol. 27, 1933, p. 4638.

The ore is subjected to the joint actions of HCl to form FeCl₃, copper chloride, nickel chloride, and H₂S, and an oxidizing agent such as air to form SO₂; the chlorides of Fe, Cu, and Ni are treated to regenerate HCl and produce oxides of Fe, Cu, and Ni. A portion of the regenerated HCl is utilized to convert the copper and nickel oxides to chlorides, which are leached out to separate them from the iron oxide. The remainder of the regenerated HCl is utilized for additional ore.

899. BALINT, ISTVAN. [Leaching Copper and Nickel Sulfide Ores.] Hungarian Patent 101,498, Feb. 15, 1930; Chem. Abs., vol. 25, 1931, p. 2406².

The ores are leached at a temperature higher than 100° C., under pressure, with FeCl₃ and CuCl₂ as solvents.

900. BJÖRLING, B. [Leaching of Sulfide Minerals Under Oxygen Pressure.] Metall., vol. 8, Nos. 19 and 20, October 1954, pp. 781-784; Metals Rev., vol. 27, No. 12, p. 28 (300-B).

The advantages and disadvantages of leaching sulfide ores of Fe, Cu, Zn, Ni, and Co under oxygen pressure, and chemical reactions of the sulfides with oxygen are discussed. Diagrams and 7 refs. are included.

901. CARON, M. H. Ammonia Leaching of Nickel Sulfide Ores; Half Century Review. Trans. Inst. Min. and Met., vol. 64, part II, 1954 and 1955, pp. 611-616; Bull. Inst. Min. Met., No. 585, 1955, pp. 611-616 (from notes of O. C. Ralston, Bureau of Mines, Washington, D. C.); Chem. Abs., vol. 49, 1955, p. 13,850d.

Miranda Malzac obtained French Patent 332,596, on May 6, 1903, which described dissolution of Ni by simultaneous oxidation with air in ammonia of the original sulfides. Geo. S. Hanes (Jour. Canadian Min.

Inst., vol. 8, 1905) discussed the solubility of copper-nickel sulfide ores in ammonia, using the Malzac process and extended it to treatment of mattes and arsenide ores. Benedict in the Linden plant in Michigan applied the process to Cu ores, followed by Kennecott after a 20-year lapse of interest. Caron visited Benedict in 1923 and applied ammoniacal ammonium carbonate to various ores of Ni and Co and applied for a Netherland patent in 1921, which was issued as No. 12,975 on March 16, 1925, although South African Patent 397 was issued in 1923.

F. A. Forward and others began publishing their work in 1948, as applied to sulfide ores without pre-roasting. Queneau and others, of International Nickel, worked on production of a high-grade iron oxide product from nickeliferous pyrite, patented in United States (Patent 2,556,215), June 12, 1951; and in 1954, announcement was made of a plant to be erected to use this process, with recovery of sulfur products in addition. The work of Chemical Construction Co. is only slightly mentioned and not documented. V. N. Ipatieff published (in Jour. Chem. Education, March 1955) his earlier work on pressure reduction of Ni and other metals from solutions by H₂.

902. FORWARD, F. A. Hydrometallurgical Process Yields Pure Metal Powders From Sulfides. Jour. Metals, vol. 5, No. 6, June 1953, pp. 775-779; Eng. Index, 1953, p. 704.

Sherritt Gordon will use an ammonia-leach, hydrogen-reduction process on Lynn Lake nickel-cobalt sulfide concentrates. Equations are given for the chemical reactions involved in ammonia leaching, copper removal, hydrolysis, and hydrogen reduction; a flow-sheet is included.

903. ——— (assigned to Sherritt Gordon Mines, Ltd.). [Extraction of Nickel From Nickeliferous Sulfide Material.] German Patent 825,747, Dec. 20, 1951 (*Cl. 40a 43.30*) (see U. S. Patent 2,576,314; Chem. Abs., vol. 46, 1952, p. 1423c); Chem. Abs., vol. 48, 1954, p. 10,521d.

904. FORWARD, F. A., AND MACKIWI, V. N. (University of British Columbia, Vancouver, Canada.). The Ammonia Pressure Process for Leaching Nickel, Copper, and Cobalt From Sherritt Gordon Sulfide Concentrates. Jour. Metals, vol. 7, Trans. AIME, vol. 203, 1955, pp. 457-463 (see Chem. Abs., vol. 48, 1954, p. 514d); Metals Rev., vol. 28, No. 5, May 1955, (47B); Chem. Abs., vol. 49, 1955, p. 5233b.

The paper relates the laboratory and pilot-plant studies that have been carried out for Sherritt Gordon Mines, Ltd. The Metallurgical Research Division is developing the NH₃ pressure leach process for extracting Cu, Ni, Co, and S from high-grade concentrate produced from Lynn Lake ores and described in some detail the chemistry of the process.

905. KISSOCK, ALAN. Extraction of Metals Such as Nickel and Cobalt. U. S. Patent 2,205,565, June 25, 1940; Chem. Abs., vol. 34, 1940, p. 7276⁹.

Direct oxidation of sulfides such as those of Ni and Co is effected in an aqueous solution containing one or more derivatives of Cl₂O, such as NaClO.

906. MEYER, R. F. (assigned to Meyer Mineral Separation Co.). Treating Ores Such as Sulfide Ores of Gold, Silver, Lead, and Zinc. British Patent 344,492, Dec. 28, 1928; Chem. Abs., vol. 25, 1931, p. 4511³.

The finely divided ore is treated with liquid, such as water (suitably after a preliminary treatment with H₂SO₄, to remove part of the Zn) only to such an extent as to render it damp or "quasi-wet" and not to interfere with the passage of air between the particles, and is then agitated with a gaseous agent such as a mixture of air and SO₂ (for the formation of ZnSO₄). Metal values are subsequently extracted

from the treated material. A tailing containing Cu and Co may be treated with water, air, and SO₂, or air and Cl₂. The process is well suited for treating manganese silicate ores and Ni and Co ores.

907. RYMERSHOLMS GAMLA INDUSTRI AKTIEBOLAG. [Treating Roasted Pyrites.] German Patent 517,748, Nov. 13, 1925, Chem. Abs., vol. 25, 1931, p. 2678.

The valuable constituents of chlorinated roasted pyrites are obtained by lixiviating the pyrites in stages with (1) lye poor in Cu but rich in Zn, containing mainly chlorides; and (2) lye poor in Zn but rich in Cu, containing mainly sulfates. Cu, Zn, Ag, Co, S, and Cl compounds are so obtained.

908. WATANABE, TOSHIO. [The Recovery of Cobalt in Cupriferous Pyrites.] Proc. World Eng. Cong., Tokyo, 1929, vol. 35, 1931, pp. 267-284; Chem. Abs., vol. 25, 1931, p. 5372⁹.

Cupriferous pyrite in Japan contains 0.05 to 0.1 percent Co. The pyrite is used for H₂SO₄ manufacture. The cinder is leached for Cu. After cementation, the waste liquor analyzes Cu 0.09 gm./l., Fe 44.98, Zn 7.21, Mn 0.14, Co 1.07, Ca 0.75, Mg 4.20, Na 65.00, sulfate 132.84, and Cl 62.36. Zinc is precipitated with H₂S; Co, Mn, and remaining Zn are precipitated with alkali polysulfide and filtered. The precipitate is given a sulfatizing roast and lixiviated, dissolving Co and a small quantity of Zn and Fe. Iron is precipitated with KClO₄ and powdered limestone. Zinc is precipitated with H₂S and Co as polysulfide. An acid washing removes impurities, after which the sulfide is oxidized to CoO. The effects of variables in each step are presented.

HYDRO TREATMENTS OF MATTE AND SPEISS

909. DOWNIE, C. C. Researches on Nickel Matte. Min. Jour., London, vol. 238, Jan. 4, 1952, pp. 12-13; Metals Rev., vol. 25, No. 3, March 1952, p. 25 (31-C).

A modification of smelting, converting, and matte-refining procedure has been developed for application to ores containing a considerable amount of Cu. An adaptation of the oxalic acid process and an electro-refining process are discussed.

910. FALCONBRIDGE NIKKELVERK AKTIESELSKAP. Extracting Nickel. British Patent 372,958, May 22, 1930; Chem. Abs., vol. 27, 1933, p. 2924.

A strongly reactive metallic Ni product, obtained by gas reduction (for example, with H₂ or other gas) of Ni compounds at a low temperature, preferably 350°-450° C., is used to neutralize the acidity and to cement the Cu present in nickel-salt solutions, below 60° C., from which Fe is subsequently removed by oxidation with air. In an application of the process, Ni-Cu matte is ground, roasted to remove S, and leached with acid for the partial removal of Cu. Part of the leached residue is reduced as above stated to obtain the nickeliferous powder; the remainder is converted to metal and cast into anodes for electrolytic purification. The electrolyte is purified by the Ni-containing powder. The exhausted nickeliferous material is mixed with the ground matte and reused.

911. HAMPRECHT, GÜNTHER (assigned to I. G. Farbenindustrie, A. G.). [Extraction of Nickel and Copper From Matte.] German Patent 680,519, Aug. 10, 1939 (*Cl. 40a 43.30*); Chem. Abs., vol. 36, 1942, p. 1885⁷.

A Ni-Cu matte is readily dissolved in cold CuCl₂ solution containing enough NiCl₂ to keep in solution all the CuCl formed. Thus, at 20° C., 220, 330, and 440 gm. NiCl₂ per l. will prevent the precipitation of 80, 170, and 225 gm. CuCl per l., respectively. Higher temperatures require correspondingly less NiCl₂. The

matte dissolves completely, except for sulfur impurities and the noble metals derived from the original ore. Mattes with high Ni content (approximately 45 percent) require a solution in which the $\text{NiCl}_2:\text{CuCl}_2$ ratio corresponds to the composition of the matte. For mattes with lower Ni content the $\text{NiCl}_2:\text{CuCl}_2$ ratio in the solution is higher than in the matte.

912. HAMPRECHT, GÜNTHER (assigned to I. G. Farbenindustrie, A. G.). Decomposition of Nickel-Copper Matte. U. S. Patent 2,186,293, Jan. 9, 1940 (*see* British Patent 506,841; Chem. Abs., vol. 34, 1940, p. 34³); Chem. Abs., vol. 34, 1940, p. 3231³.

913. HAMPRECHT, GÜNTHER, AND PAUCKNER, GUSTAV (assigned to I. G. Farbenindustrie, A. G.). Separation of Nickel and Copper in a Nickel-Copper Matte. German Patent 694,494, July 4, 1940 (*Cl. 40a 31.60*) (*see* U. S. Patent 2,180,520; Chem. Abs., vol. 34, 1940, p. 1607³); Chem. Abs., vol. 35, 1941, p. 5084³.

914. ——— (assigned to I. G. Farbenindustrie, A. G.). Separation of Nickel From Copper. U. S. Patent 2,180,520, Nov. 21, 1940; Chem. Abs., vol. 34, 1940, p. 1607³.

A Ni-Cu matte is acted upon by a CuCl_2 solution, resulting in the formation of NiCl_2 and CuCl_2 , which latter is oxidized with chlorine to CuCl_2 . The solution thus obtained is used for the treatment of further quantities of the Ni-Cu matte. A remaining portion of the solution from the matte is treated for precipitation of Cu by the addition of fresh matte.

915. HAMPRECHT, GÜNTHER, SCHLECHT, LEO, AND TRAGESER, GEORG (assigned to I. G. Farbenindustrie, A. G.). Separation of Nickel and Copper. U. S. Patent 2,223,239, Nov. 26, 1941; Chem. Abs., vol. 35, 1941, p. 1751³.

A Ni-Cu matte containing about one-fourth as much S as Cu is treated with HCl or H_2SO_4 (suitably a 20-percent HCl solution for dissolving Ni but only a small amount of Cu).

916. HARSHAW, W. J., AND HOMER, G. L. (assigned to Harshaw Chemical Co.). Obtaining Copper and Nickel From Matte. U. S. Patent 1,729,243, Sept. 24, 1929; Chem. Abs., vol. 23, 1929, p. 5149.

The matte is ground to about 10-mesh and leached with hot dilute H_2SO_4 ; the residue is ground, roasted to about 400° C., and leached with dilute H_2SO_4 . Fresh matte is added to make up the weight to about that of the original batch, the mixture is leached with dilute H_2SO_4 , again mixed with fresh matte to bring the weight up to about that of the original batch, and the mixture is further leached with dilute H_2SO_4 . The re-roastings of the residue tend to solubilize its Cu and Ni content and to facilitate complete recovery of these metals.

917. I. G. FARBENINDUSTRIE, A. G. Separating Nickel Salts From Solution. British Patent 498,152, Jan. 4, 1939; Chem. Abs., vol. 33, 1939, p. 4387³.

Ni salts are separated from solutions containing other heavy metals, especially Fe and Cu, for example, solutions obtained by lixiviation of Cu-Ni mattes containing Fe with acids, by precipitation as NiCl_2 by concentrated HCl. Any unoxidized Fe is first treated by passing Cl_2 into the solution or by other oxidation means, and precipitated by CaCO_3 .

918. ———. Decomposing Nickel-Copper Matte. British Patent 508,841, June 6, 1939; Chem. Abs., vol. 34, 1940, p. 34³.

The matte is decomposed with a CuCl_2 solution containing enough NiCl_2 to keep the Cu_2Cl_2 formed in solution. From the solution obtained, Cu and Ni may be separated electrolytically. The decomposing solutions may be re-formed with Cl_2 obtained from electrolytic

deposition of Ni. The Ni content may be adjusted if necessary.

919. ———. Separation of Nickel or Cobalt and Copper. British Patent 512,079, Aug. 29, 1939; Chem. Abs., vol. 35, 1941, p. 69³.

Ni or Co is recovered apart from the Cu by treating with acid a Ni-Cu or Co-Cu matte having an S content less than one-third and more than one-fifth of the Cu content. The acid is preferably aqueous HCl.

920. ———. [Separating Nickel and Copper From Matte.] French Patent 846,479 Sept. 18, 1939 (*see* British Patent 506,841; Chem. Abs., vol. 34, 1940, p. 34³); Chem. Abs., vol. 35, 1941, p. 1018³.

921. JOHNSON, G. W. (assigned to I. G. Farbenindustrie, A. G.). Separation of Nickel Salts From Solutions Containing Other Heavy Metals. British Patent 498,152, Aug. 3, 1937; British Chem. Abs., 1939, p. B-481.

Acid liquor from the lixiviation of Ni matte is treated with Cl_2 to oxidize Fe^{2+} , then saturated with HCl gas to precipitate NiCl_2 , which is removed, and the mother liquor is used for further lixiviation.

922. ——— (assigned to I. G. Farbenindustrie, A. G.). Decomposition of Nickel-Copper Matte. British Patent 506,841, Jan. 12, 1938; British Chem. Abs., 1939, p. B-848.

The matte is leached with aqueous CuCl_2 containing enough NiCl_2 to keep in solution any Cu_2Cl_2 that may be formed.

923. ———. Separation of (A) Nickel or Cobalt and Copper, and (B) Nickel and Copper. British Patents (A) 512,079, May 20, 1938, and (B) 512,347, Apr. 28, 1938; British Chem. Abs., 1939, p. B-1254.

(A) Mattes containing Ni and Cu with S=20 to 33 percent of the Cu content are treated with 20 percent aqueous HCl, whereby the greater part of the Ni is dissolved; for example, the extract from a matte containing Ni 43.4, Cu 45.9, and S 9.2 percent contains 92 percent of the Ni content and 0.2 percent of the Cu. (B) Matte containing approximately Ni 50, Cu 27, and S 22 percent is leached with a solution containing Cu (as CuCl_2) and Ni (as NiCl_2) and the extract containing Cu (as CuCl_2) and Ni is divided. One portion containing Cu is chlorinated and used for treating fresh matte; the other, diluted with H_2O , is treated with matte (Ni 43, Cu 47, and S 8 percent) 3 parts, which precipitates the Cu content. The Ni is recovered from the mother liquor by electrolysis, the regenerated Cl_2 being used again.

924. LATHE, F. E. A Proposed Nickel-Refining Process. Canadian Chem. Met., vol. 13, 1929, pp. 174-176; Chem. Abs., vol. 23, 1929, p. 3882³.

A short account of the Orford and Mond processes is followed by Lathe's modification of the sulfuric-acid process. When 3 percent of Fe is left in the converter matte and the latter granulated in water to produce a fine crystal structure, it is possible, on grinding to 80-mesh, to dissolve 99 to 99.9 percent of the Ni in "30-percent" H_2SO_4 at 80°-100° C. and still leave all of the Cu in the insoluble residue. S can be recovered from the liberated H_2S . The Fe is removed from the NiSO_4 solution by oxidation of part of the latter in a cyclic process and precipitation by Ni(OH)_2 . From the Ni solution, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ is crystallized out, dehydrated at 300° C., decomposed at 800° C., and reduced by petroleum coke in a reverberatory furnace. The CuS is melted, blown in a converter, and electrolyzed. The precious metals are recovered in a very concentrated slime. In dissolving the Ni from the matte, a counter-current flow is recommended, in which the fresh matte comes in contact with a solution of low acidity and high NiSO_4 content, while the nearly exhausted matte comes in contact with the strongest acid to remove the last

traces of Ni. Traces of Cu dissolved by the strong acid are later precipitated when the solution comes in contact with the fresh matte. The process in a single operation gives an almost quantitative separation of the Ni from the Cu and the precious metals. It provides for recovery of the Ni and Cu in a condition of high purity, for recovery of S as a byproduct, and for recovery of the precious metals in a very concentrated form. No chemicals need be purchased, since the H_2SO_4 is regenerated and the small quantity of $\text{Ni}(\text{OH})_2$ required is made in the plant by electrolysis.

925. LATHÉ, F. E. Treating Copper-Nickel Matte. British Patent 303,066, Dec. 27, 1927 (*see Chem. Abs.*, vol. 22, 1928, p. 2735); *Chem. Abs.*, vol. 23, 1929, p. 4435².

Various details of refining Cu-Ni matte and auxiliary treatments for recovery of precious metals, etc., are described.

926. —. Refining Copper-Nickel Matte. U. S. Patent 1,756,092, Apr. 29, 1930 (*see Chem. Abs.*, vol. 23, 1929, p. 4435); *Chem. Abs.*, vol. 24, 1930, p. 2076².

A substantial quantity of iron sulfide is retained in the matte; it is rapidly cooled to increase the rate and completeness of dissolution of the nickel sulfide constituent in acid.

927. MAKISHIMA, GENICHIRO, AND HORINO, ICHIHIEI. [The Production of Nickel and Cobalt From Nickel Speiss.] *Jour. Electrochem. Soc. Japan*, vol. 21, 1953, pp. 239-241; *Chem. Abs.*, vol. 47, 1953, p. 12,175f.

Nickel speiss from Burma containing Ni 26, Co 4, Cu 10, Pb 7, As 40 percent, and Sb, Sn, and Fe was chlorinated and the solution treated with lime, then with hydrogen sulfide to remove As, Sb, Cu, and Pb as oxides and sulfides. Milk of lime was added to the mixture in the presence of Cl_2 to remove Co in the form of cobaltic hydroxide; the remaining solution was neutralized by an alkali to give nickelous hydroxide, which was reduced to Ni metal in an electric furnace.

928. PRASAD, MATA, AND TENDULKAR, M. G. The Action of Sulfuric Acid on Nickel-Copper Matte. *Jour. Chem. Soc.*, 1931, pp. 1407-1411; *Chem. Abs.*, vol. 25, 1931, p. 5107¹.

Experiments were made to determine the cause of the insolubility in H_2SO_4 of NiO in Cu-Ni mattes obtained by roasting Ni ores. The action of 0.1 N H_2SO_4 on mixtures of (a) $\text{CuO-Ni}_2\text{O}_3$, (b) CuO (prepared at 800° C.), and NiO (prepared at 400°-1,000° C.), and (c) the oxides obtained by heating an equimolecular mixture of $\text{Ni}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ were studied. The investigations led to the conclusion that during the roasting of the ore nearly all the Ni is converted into the inactive form of NiO . This accounts for the insolubility in H_2SO_4 of the NiO contained in the Ni-Cu matte. It is also probable that during the roasting of the ore the complex oxide $\text{CuO} \cdot 4\text{NiO}$ is formed, which is virtually insoluble in H_2SO_4 . It is shown that Ni is dissolved much more readily from $\text{CuO} \cdot \text{Ni}_2\text{O}_3$ mixtures by H_2SO_4 solutions than from $\text{NiO} \cdot \text{CuO}$ mixtures. In the latter mixtures, the quantity of Ni dissolved decreases with the increase in the temperature of preparation of NiO , increases with increase in H_2SO_4 temperature, and is not affected by change in the ratio of $\text{NiO}:\text{CuO}$ in the mixture.

928a. SCHOPPER, WALTER (assigned to Norddeutsche Affinerie). Treating Crude Speisses Containing Nickel and Cobalt, Arsenic, Antimony and Various Other Metals. U. S. Patent 1,863,807, June 21, 1932 (*see German Patent* 545,836; *Chem. Abs.*, vol. 26, 1932, p. 3476); *Chem. Abs.*, vol. 26, 1932, p. 4294.

929. SMITH, S. C. Treating Materials Containing Nickel and Copper. British Patent 311,909, Apr. 18, 1929; *Chem. Abs.*, vol. 24, 1930, p. 816².

Leached or unleached roasted ferruginized or bessemerized matte or other material containing Ni and Cu

is reduced to obtain a metal sponge, and the latter is moistened with acid such as H_2SO_4 or HCl and exposed to the air until a rise in temperature occurs. By this treatment, the Ni and Cu, and Fe and Co, if present, are converted into acid-soluble compounds. When precious metals, such as Au, Ag, and metals of the Pt group, are present, they remain in the residue and may be concentrated in successive operations.

930. UDY, M. J. Recovery of Metallic Salts From Matte. U. S. Patent 2,424,866, July 29, 1947; *Chem. Abs.*, vol. 41, 1947, p. 6520e.

If the proportion of sulfur to metals in a finely divided matte does not exceed an atom-to-atom basis, enough H_2SO_4 may be added to dissolve and neutralize the iron present; H_2S generated maintains Cu and Ni in an insoluble state; after the removal of Fe, the insolubles may be roasted and Ni and Co salts produced by action of an acid.

931. — (assigned to Guaranty Investment Corp., Ltd.). The Treatment of a Matte to Recover Metallic Salts. U. S. Patent 2,612,441, Sept. 30, 1952; *Chem. Abs.*, vol. 47, 1953, p. 470a.

Zn and other nonferrous metals, particularly Ni and Cu, are separated from Fe in iron sulfide ores by (1) smelting with calcium carbonate, ferric oxide, and carbon to produce a sulfide matte; (2) grinding the matte to 100-105 mesh; (3) dissolving the Fe with 10 to 20 percent H_2SO_4 at 70°-100° F. in a countercurrent system comprising a series of receptacles to produce a neutral solution of ferrous sulfate and a solid residue containing Zn and other nonferrous metals as sulfides. The temperature is so controlled that the liquid remains saturated with H_2S , precipitating most of the Zn.

932. —. Improvements in Metallurgy. U. S. Patent 2,609,272, Sept. 2, 1952 (*Chem. Abs.*, vol. 47, 1953, p. 470b); British Patents 656,140 (*Chem. Abs.*, vol. 46, 1952, p. 5798i), 656,141 (*Chem. Abs.*, vol. 46, 1952, p. 5513i), 656,142 (*Chem. Abs.*, vol. 46, 1952, p. 5514a), 656,143 (*Chem. Abs.*, vol. 46, 1952, p. 5514b), and 656,144 (*Chem. Abs.*, vol. 46, 1952, p. 5514c).

Ni, Cu, and Zn are separated from Fe by (1) subjecting the matte to repeated treatments with aqueous H_2SO_4 in a countercurrent system including at least four receptacles and forming residues in each successive receptacle, including progressively diminishing proportions of soluble FeS ; (2) employing the aqueous acid initially to treat the residue containing a small amount of soluble FeS and large amounts of other metal sulfides; (3) thereafter treating a residue containing larger amounts of soluble FeS ; and finally (4) treating raw material, thereby forming solutions in successive receptacles containing diminishing amounts of FeSO_4 . The process is controlled to have neutral FeSO_4 substantially free from Ni, Cu, and Zn in one receptacle and Fe-free Ni, Cu, and Zn in another receptacle. Ni, Cu, and Zn are separated by appropriate procedure. (*See British Patent* 656,142.) Ferrous sulfate is roasted to Fe_2O_3 , which is reduced to Fe. The temperature of the H_2SO_4 digesting treatment is controlled to prevent loss of enough H_2S to render other sulfides soluble in FeSO_4 , for example, Ni or Co separation at 50°-100° C. for approximately 80 min., Cu at 150° C. maximum for 90 min., and Zn at 25°-50° C. As described in British Patent 656,143. Zn is recovered from the insoluble portion mentioned in British Patent 656,141 by crystallization of ZnSO_4 or ZnS , or mixtures of the two, by maintaining a concentrated and substantially neutral solution of FeSO_4 , which is saturated with H_2S . If CuS is present, its sulfide is precipitated, along with ZnS , and is separated subsequently by heating the sulfide mixture in H_2SO_4 under oxidizing conditions to form an acid solution of ZnSO_4 and CuSO_4 . Copper sulfide is precipi-

tated with H_2S from the digesting treatment. (See British Patent 656,144.) In the treatment of ores described in British Patent 656,140, conditions of concentration and temperature $50^\circ\text{--}100^\circ\text{C}$., during digestion are controlled to produce a solution of FeSO_4 of predetermined composition to recrystallize $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ below 25°C ., and to reuse the mother liquor, along with the H_2SO_4 , for further digestion.

933. WEST, DE W. H., AND WALLIS, A. E. (assigned to Mond Nickel Co., Ltd.). Production of Nickel or Cobalt Sulfate. British Patent 672,993, July 9, 1949; British Abs., 1952, p. B-1-1713.

Calcined and reduced Ni matte is treated with H_2SO_4 to yield a neutral or faintly acid liquor containing NiSO_4 and FeSO_4 , with or without CoSO_4 . The liquor at not less than 80°C . is aerated with an oxidizing gas mixture containing 0.5 to 3.0 volume-percent of SO_2 to convert all the FeSO_4 into $\text{Fe}_2(\text{SO}_4)_3$, and a Ni base is then added to precipitate $\text{Fe}(\text{OH})_3$.

PRECIPITATION AND SEPARATION

934. MACKIW, V. N. (assigned to Sherritt Gordon Mines, Ltd.). Separating Metal Values From Ammoniacal Solution. U. S. Patent 2,693,404, Nov. 2, 1954; Chem. Abs., vol. 49, 1955, p. 1524c.

Metals of the group Cu, Ag, Au, Pt, Pd, and Os, whose sulfides are associated with but are less soluble than those of Ni and Co, are removed from ammoniacal solutions of the latter in the presence of polythionate and thiosulfate ions by boiling the solution to reduce the NH_3 content, whereupon the less soluble sulfides precipitate to give a Ni-Co solution of high purity. In the treatment of Ni-Co sulfide ores by leaching in ammoniacal solution under O_2 pressure, advantage can be taken of the maximum occurring in the polythionate concentration as leaching progresses, the best separation being obtained by boiling a leach solution containing a weight ratio of polythionate and thiosulfate-S to Cu between 0.8 and 1.2.

935. MCGAULEY, P. J. (assigned to Chemical Construction Co.). Recovery of Copper and Nickel From Floation Concentrates. U. S. Patent 2,647,827, Aug. 4, 1953; Chem. Abs., vol. 47, 1953, p. 10,447h.

Cu-bearing ores or concentrates containing Ni, Co, and/or Fe and at least some sulfides are subjected to an acidic oxidation leach in the presence of $\text{Fe}_2(\text{SO}_4)_3$ to convert the metals to sulfates. The solution is filtered, and NH_3 is added to precipitate $\text{Fe}(\text{OH})_3$. Ammonium sulfate and additional NH_3 are added to precipitate Ni and/or Co and to separate these metals from Cu. Precipitation of Co requires a pH of 3.5 to 5.5 and precipitation of Ni 5.5 to 6.4. Operating temperatures are $25^\circ\text{--}125^\circ\text{C}$.

936. SVELSBERG, WALTER. [Precipitation of Copper by Nickel Matte.] Metall. u. Erz., vol. 30, 1933, pp. 445-448; Chem. Abs., vol. 28, 1934, p. 1309^b.

In the precipitation of Cu from solution by Ni matte, the metallic part of the Ni matte is not effective, but the Cu is precipitated as sulfide by the sulfidic part of the matte. X-ray analysis confirms this.

STUDIES; EQUILIBRIA; SOLUTIONS; STRUCTURE OF SALTS AND METALS

AMMINES AND AMMONIA COMPOUNDS

937. ALBI CHEMICAL CORP. Complex Metal Ammine Salts. British Patent 605,851, Aug. 3, 1948; Chem. Abs., vol. 43, 1949, p. 3158a.

Salts consisting of ammonia joined with a primary metal cation (such as Ni, Co, or other metals) are produced by dry mixing and agitation of a solid noncomplex metal salt with a nonaqueous source of ammonia (such as ammonium carbonate, urea, amines), drying and grinding to size. In an example, $\text{CuSO}_4 \cdot 45$, $(\text{NH}_4)_2\text{CO}_3$ 50, and NaF 16 parts were mixed dry. When CO_2 was no longer evolved, the product was dried and ground.

938. BAILAR, J. C., JR., AND CLAPP, L. B. The Preparation and Properties of Inorganic Coordination Compounds. I. The Action of Some Organic Amines Upon Dichloro-diethylene Diamine Cobaltic Chloride. Jour. Am. Chem. Soc., vol. 67, 1945, pp. 171-175. Chem. Abs., vol. 39, 1945, p. 1365^b.

The reactions of cis- and trans- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ with the following amines were studied: PhNH_2 , p-toluidine, o-toluidine, o-anisidine, p-phenetidine, pyridine, MeNH_2 , EtNH_2 , iso- PrNH_2 , allylamine, sec- BuNH_2 , 2, 4, 6, trichloroaniline, M-nitroaniline, quinoline, and PhMeNH_2 . Except for the last four amines, which cause rearrangement and disproportionation, the amines form compounds of the type $[\text{Co}(\text{en})_2(\text{RNH}_2)_2]\text{Cl}_2$. The products seem to be the same, whether prepared from cis- or trans-dichloro salt.

939. BAILAR, J. C., JR., AND WORK, J. B. Role of Catalysis in the Preparation and Reactions of Cobaltic and Chromic Ammines. Jour. Am. Chem. Soc., vol. 67, 1945, pp. 176-179; British Abs., 1945, p. A-1-204.

940. BJERRUM, JANNIK. Metal Ammine Formation in Aqueous Solutions. Theory of Reversible Step Reactions. Separate publication by P. Haase & Son, Copenhagen, 1941, 298 pp. (in English) (see Chem. Abs., vol. 26, 1934, p. 2364; vol. 27, 1933, p. 36; and vol. 29, 1935, p. 67^a); Chem. Abs., vol. 35, 1941, p. 632^c.

The formation of metal ammines in aqueous solution is treated as a statistical problem involving the formation of all intermediate steps. Modification is then made for steric effects where positions which the group might occupy are not equivalent, and for the effect of ligands present upon the incoming group. Data are given for ammine formation in ammoniacal solution and also in solutions of ethylenediamine for nickel and cobaltous and cobaltic ions and other metal ions.

941. BONTKE-NAESS, G., AND HASSEL, O. Atomic Distances in Werner Intercalated Compounds. II. Some Hexamino- and Hexamethylamine-Halides of Bivalent Nickel and Bivalent Cobalt of the Fluorite Type.] Ztschr. anorg. allgem. Chem., vol. 211, 1933, pp. 21-27 (see Chem. Abs., vol. 27, 1933, p. 2618); Chem. Abs., vol. 27, 1933, p. 3892.

942. BOKII, G. B., AND GILINSKAYA, E. A. Structure of the Complex Ion $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$. Bull. Acad. Sci., U. S. S. R., Div. Chem. Sci., 1953, pp. 227-229 (English trans.) (see Chem. Abs., vol. 48, 1954, p. 3736f); Chem. Abs., vol. 48, 1954, p. 12,496c.

943. BRIGAND, JEAN. [Comparative Study of Some Complex Bases.] Compt. rend., vol. 206, 1938, pp. 1467-1469; Chem. Abs., vol. 32, 1938, p. 4899^f.

Titration curves of hexamino-triethylenediamino- and tripropylenediamino-cobaltic hydroxides were determined electrometrically with the glass electrode and conductometrically; results were checked by examination of the ultraviolet absorption spectra. All three bases behave similarly and are very much stronger than the simple amines they contain, which differ markedly among themselves.

944. ———. [The Preparation of Cobalt. III. Hexamine Complexes.] Compt. rend., vol. 225, 1947, pp. 1319-1320; Chem. Abs., vol. 42, 1948, p. 3725d.

No example is known of a cobalt ammine compound in which the NH_3 has been replaced, molecule for molecule,

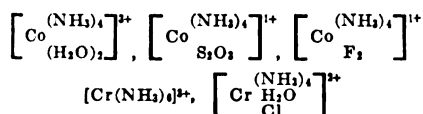
by a monoamine; the only monoamine complexes previously known contained a single molecule of the ammine.

945. Brintzinger, H., and Osswald, H. [A New Group of Complex-Compounds: Complex Compounds Whose Central Ion Is a Complex Cation. IV. Two-Shell Arsenato Complex Compounds With Complex Cobalt Cations as Central Ions.] *Ztschr. anorg. allgem. Chem.*, vol. 225, 1935, pp. 365-368 (*see Chem. Abs.*, vol. 30, 1936, p. 981⁴); *Chem. Abs.*, vol. 30, 1936, p. 2515⁷.

Arsenate ions form tetra-arsenato-cobaltamine anions with cobaltamine cations as central ions. The structure of these ions is found by ion weight determinations by the dialysis method.

946. ———. [Complex Amines of Trivalent Metals.] *Ztschr. anorg. allgem. Chem.*, vol. 224, 1935, pp. 280-282; *Chem. Abs.*, vol. 30, 1936, p. 696⁷.

Determination of the atomic weight by dialysis establishes the composition of certain complex Co and Cr cations as follows:



It is also demonstrated that the triethylenediamine cobaltic ion is dimeric and therefore has the composition $\text{Co}_2[\text{C}_2\text{H}_4(\text{NH}_2)_2]_6^{4+}$.

947. CERNATESCU, R., and PONI, M. P. [Amino Bisulfites of Cobalt (II) and Nickel.] *Bull. sec. sci. acad. roumaine*, vol. 25, 1943, pp. 453-458 (in French); *Chem. Zentralb.*, vol. II, 1944, pp. 103-104; *Chem. Abs.*, vol. 39, 1945, p. 4015¹.

Detailed directions are given for preparing $[\text{Ni en}]_2[(\text{HSO}_3)_2\text{en}]$ (I), and di-p-anisidinecobalt bisulfite $[\text{Co}(\text{p-C}_6\text{H}_4(\text{OCH}_3)_2\text{NH}_2)_2](\text{HSO}_3)_2$ (II).

948. CHATELET, MARCEL. [Calorimetric Study of the Action of Ammonia on Cobalt Chloride in Water in the Presence of Ammonium Chloride.] *Jour. chim. phys.*, vol. 33, 1936, pp. 313-324; *British Chem. Abs.*, 1936, p. A-797.

949. ———. [System Cobalt Chloride-Ammonium Chloride-Ammonia-Water.] *Compt. rend.*, vol. 202, 1936, pp. 216-217; *Chem. Abs.*, vol. 30, 1936, p. 1680⁷.

950. ———. [Partial Precipitation of Cobalt by Ammonia in Excess and Formation of Cobaltamine Ion.] *Compt. rend.*, vol. 204, 1937, pp. 764-766 (*see Chem. Abs.*, vol. 30, 1936, p. 5112¹); *Chem. Abs.*, vol. 31, 1937, p. 3366⁹.

Experiments in which the amount of CoCl_2 varied from 0.01 to 0.1 M, of NH_3 from 0.25 to 2.5 M, and of NH_4Cl from 0 to 0.28 M show that the reactions between Co^{++} and NH_3 in no way depend on the concentration of NH_4Cl . The hindrance of the precipitation of Co^{++} by NH_4Cl does not depend solely on the pH.

951. DERR, P. F., and VOSBURGH, W. C. Complex Ions. VII. A Solubility Method for Determining the Instability Constants in Solutions and the Amines of Nickel, Cadmium, and Magnesium. *Jour. Am. Chem. Soc.*, vol. 65, 1943, pp. 2408-2411; *British Abs.*, 1944, p. A-1-127.

952. DUVAL, RAYMONDE. [Cobaltipentammines.] *Ann. chim.*, vol. 18, 1932, pp. 241-301 (*see Chem. Abs.*, vol. 27, 1933, p. 475); *Chem. Abs.*, vol. 27, 1933, p. 1291.

953. EDWARDS, L. J. (University of North Dakota, Grand Forks). New Complexes of Cobalt and Nickel With Certain Diamines. *Proc. North Dakota Acad. Sci.*, vol. 4, 1950, pp. 30-32; *Chem. Abs.*, vol. 45, 1951, p. 2359g.

A list of Ni and Co complexes is appended, with their preparation. The N-alkyl complexes are much

more easily decomposed by refluxing with concentrated acids than are the N-alkylol complexes; the nickel complexes are less stable than the cobalt complexes.

954. ERLIENMEYER, H., and SCHMID, E. H. [Structural Chemistry. III. Amine Complexes of Thiazole and Bethiazole.] *Helv. chim. acta*, vol. 24, 1941, pp. 869-877 (*see Chem. Abs.*, vol. 33, 1939, p. 8612⁷; vol. 35, 1941, p. 2436⁵); *Chem. Abs.*, vol. 36, 1942, p. 4433⁵.

New complex compounds of thiazole and thiazole derivatives with Ni, Co, and other metal ions have been prepared to allow comparison with the corresponding pyridine compounds. Directions are given for preparing the metal thiazole chloride salts. Two modifications of the cobalt salt, α and β varieties, represent cis- and trans-isomers.

955. FERNELIUS, W. C., and OTHERS. *Inorganic Syntheses*, vol. II, 1946, 294 pp. *Chem. Abs.*, vol. 40, 1946, pp. 7029⁹ and 6009⁵.

Bjerrum, Jannik and McReynolds, J. P. Hexammine Cobalt. III. Salts, pp. 216-221.

A. Hexammine Cobalt (III) Chloride Method I (*see Bjerrum, Jannik, Chem. Abs.*, vol. 35, 1941, p. 6534¹).

B. Hexammine-Cobalt (III) Nitrate Method I (*see Bjerrum, Jannik, Chem. Abs.*, vol. 35, 1941, p. 6534²). Method 2 is discussed.

Work, J. B. Tris (Ethylenediamine) Cobalt (III) Chloride, pp. 221-222.

Bailar, J. C., Jr. Cis- and Trans-Dichlorobis (Ethylenediamine) Cobalt (III) Chloride and the Resolution of the Cis Form, pp. 222-225.

Bigelow, J. H. Potassium Hexacyanocobaltate (III), pp. 255-257.

Fernelius, W. C., and Burbage, J. J. Potassium Tetraacyanonickelate (II), pp. 227-228.

Gilliland, W. L., and Blanchard, A. A. Nickel Tetracarbonyl, pp. 234-237.

Goldberg, Paul, and Blanchard, A. A. Dicobalt-Octacarbonyl, Cobalt-Nitrosyl-Tricarbonyl, and Cobalt-Tetracarbonyl-Hydride, pp. 238-243.

956. GARRICK, F. J. Redetermination of the Solubility of Chloropentammine Cobaltic Chloride. *Nature*, vol. 136, 1935, pp. 1027-1028; *British Chem. Abs.*, 1936, p. A-282.

The compound, purified by an improved method (*British Chem. Abs.*, 1935, p. A-1335) gave 0.00925 and 0.0211 gram-molecules per liter at 20° and 25° C., respectively.

957. GARRICK, F. J., ANDERSON, J. S., SPOOR, N. L., and BRISCOE, H. V. A. Possible Acid-Dissociation of Metal-Ammonia Ions, and Its Bearing on Certain Reactions. *Nature*, vol. 139, 1937, pp. 507-508; *British Chem. Abs.*, 1937, p. A-1-248.

958. GELOSO, M., and LEVY, I. S. [Influence of Ammonia on the Adsorption of Copper and Nickel Salts.] *Compt. rend.*, vol. 189, 1929, pp. 175-177; *Chem. Abs.*, vol. 23, 1929, p. 4864⁹.

959. GERMAN, W. L., and JAMSETT, R. A. The Formation of Certain Amines. *Jour. Chem. Soc.*, 1939, pp. 1337-1341 (*see Chem. Abs.*, vol. 32, 1938, p. 8294⁹); *Chem. Abs.*, vol. 34, 1940, p. 1583².

The reactions between salts and NH_3 in solutions in MeOH and EtOH resemble those between solid salts and gaseous NH_3 rather than those that occur in aqueous salt solutions with ammonium hydroxide. The following compounds were found in MeOH: $\text{CoCl}_2 \cdot 2\text{NH}_3$, $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$ and compounds with other metals; in EtOH $\text{CoCl}_2 \cdot 2\text{NH}_3$ and $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$.

960. ———. Studies in Ionization in Nonaqueous Solvents. IV. The Formation of Certain Amines in Methyl and Ethyl Acetates and in Acetone. *Jour. Chem. Soc.*, 1940, pp. 1360-1362 (*see Chem. Abs.*, vol. 34, 1940, p. 1583¹); *Chem. Abs.*, vol. 35, 1941, p. 998⁶.

961. GRANDPERRIN, MARCELLE. [A New Carbonate of Nickle (II) Amine.] *Bull. soc. chim.* (5), vol. 5, 1938, pp. 1712-1713; *Chem. Abs.*, vol. 33, 1939, p. 2059⁹.

Deep-violet crystals separated from a dilute alcoholic ammoniacal solution in contact with Raney Ni. Exposure to air caused the crystals to lose some NH_3 and change in color to blue and then green. Analysis of the crystals agrees fairly well with the suggested formula $\text{NiCO}_3 \cdot 5\text{NH}_3 \cdot 4\text{H}_2\text{O}$. The green salt agrees with the formula $2\text{NiCO}_3 \cdot 3\text{NH}_3$ and can also be prepared from NiCO_3 and NH_3 . These complexes can be prepared by suspending NiCO_3 in NH_4OH and introducing NH_3 .

962. HÜTTIG, G. F. AND KOLLMAN, O. [Ammines Which Are Stable Only in the Supercritical Region of Ammonia.] *Mh. Chem.*, vol. 82, 1951, pp. 735-741; *British Abs.*, 1952, p. A-1-633.

Isocohores marking the pressure-temperature limits for the existence of the various amines of FeCl_3 , NiCl_2 , and MnCl_2 have been determined. The method of investigation was to add an excess of NH_3 to the anhydrous salt in an autoclave at a controlled temperature and to record the pressures after measured amounts of NH_3 are released. The following previously unknown amines were found to exist above the critical pressure-temperature conditions for NH_3 : FeCl_3 with 7 and 8 NH_3 ; NiCl_2 with 7, 9, and 10 NH_3 ; and MnCl_2 with 4, 7, 8, 10, 11, and 12 NH_3 .

963. HYNES, W. A., YANOWSKI, L. K., AND SHILLER, MORRIS. Modified Method for the Preparation of Monochloropentammine Cobaltic Chloride (Purpureocobaltic Chloride). *Jour. Am. Chem. Soc.*, vol. 60, 1938, pp. 3053-3054; *Chem. Abs.*, vol. 33, 1939, p. 3715⁹.

Purpureocobaltic chloride has been prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, using H_2O_2 as oxidant in the presence of NH_4Cl . A much better yield is obtained in a shorter time than by the ordinary method.

964. JOB, PAUL, AND BRIGANDO, JEAN. [Diethylenetriamine Complexes.] *Compt. rend.*, vol. 210, 1940, pp. 438-440 (*see Chem. Abs.*, vol. 32, 1938, p. 4899⁹); *Chem. Abs.*, vol. 34, 1940, p. 3610⁹.

By the interaction of diethylenetriamine (dien) and purpureocobaltic chloride, NH_3 is evolved, and a brownish red solution is formed, whence EtOH precipitates a yellow compound, $[\text{Co}(\text{dien})_2]\text{Cl}_2$.

965. JOB, PAUL, AND TAO, L. O. [Acid Sulfates of Aquopentammine-Cobalt and of the Diaquotetrammine (complex).] *Compt. rend.*, vol. 189, 1929, pp. 641-642; *Chem. Abs.*, vol. 24, 1930, p. 800⁹.

966. KING, H. J. S., CRUSE, A. W., AND ANGELL, F. G. Amines. VI. Nickelamine Salts in Aqueous Solution. *Jour. Am. Chem. Soc.*, 1932, pp. 2928-2931 (*see Chem. Abs.*, vol. 26, 1932, p. 3744); *Chem. Abs.*, vol. 27, 1933, p. 1291.

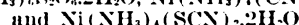
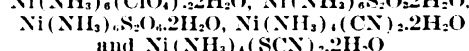
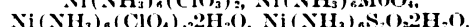
967. KOCIS, E. J. [Complex Nickel Amines.] *Magyar Chemical Folyoirat*, vol. 34, 1928, pp. 33-39; *Chem. Abs.*, vol. 23, 1929, p. 788⁹.

Examination of complex Ni hexammines shows that the concentrations of solutions or mixtures has some relation to the structure of the complex compound formed. A compound containing 2 molecules of water is formed from the 10- to 15-percent solutions, another containing 1 molecule of water from 30- to 40-percent solutions, and an anhydrous compound from a solution of 50 percent or more concentration. Nickel hexamine chlorides, bromides, iodides, nitrates, sulfates, and chromates have been examined.

968. ———. [Nickelamine Complexes: IV. Simple Nickel Hexamine and Tetrammine Compounds With Water of Hydration.] *Magyar Chemical Folyoirat*, vol. 40, 1934, pp. 147-150 (*see Chem. Abs.*, vol.

- 23, 1929, p. 4633); *Chem. Abs.*, vol. 29, 1935, p. 3622⁹.

The color and crystalline form are given for $\text{Ni}(\text{NH}_3)_6(\text{ClO}_4)_2$, $\text{Ni}(\text{NH}_3)_4\text{MoO}_4$.



969. LAMB, A. B., AND MYSELS, K. J. The Carbonate and Bicarbonate Pentammine Cobaltic Ions. *Jour. Am. Chem. Soc.*, vol. 67, 1945, pp. 468-480; *Chem. Abs.*, vol. 39, 1945, p. 1816⁹.

970. LAMB, A. B., AND STEVENS, R. G. The Constitution of Certain Cobaltamine Bases. *Jour. Am. Chem. Soc.*, vol. 54, 1932, pp. 2643-2653 (*see Chem. Abs.*, vol. 16, 1922, p. 671, and vol. 17, 1923, p. 915); *Chem. Abs.*, vol. 26, 1932, p. 4548.

By conductometric titration of several normally polyvalent ammine bases prepared from aqueous ammine bromides, it is shown that the complexly held water molecules have been completely displaced by an equivalent number of OH ions. The apparent ionizations of the OH groups remaining outside of the complex are high and are nearly identical, irrespective of the nature of the central atom, the coordination groups, and the valence of the cation. Replacement of the completely held H_2O molecules is not, however, universally complete. Interaction between aqueous ions and OH ions is comparable to that between aqueous ions and anions in general, although the replacement of H_2O molecules by OH is relatively extensive and the attainment of equilibrium is unusually rapid.

971. ———. The Aquation of Carbonate Pentammine Cobaltic Bromide. *Jour. Am. Chem. Soc.*, vol. 61, 1939, pp. 3229-3233; *Chem. Abs.*, vol. 34, 1940, p. 342⁹.

972. LEVY, L. S. [The Probable Role of the Complex Ammonias in the Adsorption of Salts of Copper and Nickel by Ferric Hydroxide.] *Compt. rend.*, vol. 189, 1929, pp. 426-428 (*see Chem. Abs.*, vol. 23, 1929, p. 4864); *Chem. Abs.*, vol. 24, 1930, p. 539.

The fact that NH_3 has considerable influence on the adsorption of Cu and Ni salts by $\text{Fe}(\text{OH})_3$ was confirmed. The shape of the adsorption curves is noticeably altered for concentrations of NH_3 greater than 6 times that of Cu or Ni, whose coordination numbers are 6. The NH_3 functions according to its concentration to form and stabilize complex salts. An excess of NH_3 serves only to alter the pH of the medium. The results obtained confirm the previous conclusion of Geloso (*Chem. Abs.*, vol. 21, 1927, p. 2409) that the course of adsorption is independent of the nature of the substance adsorbed.

973. PARIS, R. [Preparation of Nickel-Ammine Bases.] *Compt. rend.*, vol. 232, 1951, pp. 1421-1422; *British Abs.*, 1952, p. A-1-499.

A mauve crystalline compound $\text{Ni}(\text{NH}_3)_4(\text{OH})_2 \cdot \text{SiH}_4$ is obtained by saturating at 1:1 by volume mixture of EtOH and H_2O with 10-N, NH_3 and $\text{Ni}(\text{OH})_2$ at room temperature and cooling the solution to about 20° C. The crystals dissociate rapidly in air forming a blue compound $\text{Ni}(\text{NH}_3)_4\text{OH}_2$, which also slowly dissociate into $\text{Ni}(\text{OH})_2$ and NH_3 .

974. Pozzi-Escot, EMM. [Action of Ethanolamines on Solutions of Various Metallic Salts: Salts of Copper, Mercury, Cadmium, Cobalt, and Nickel.] *Rev. chim. (Peru)*, vol. 40, No. 424, 1938, pp. 303-307; *Chem. Abs.*, vol. 33, 1939, p. 1620⁹.

Describes action of commercial triethenolamine on series of metallic salts. The action is nearer that of caustic alkali than NH_3 . There is a reduction in the case of certain Hg salts.

975. PUENTE, H. A., AND LELONG, A. L. M. [Conductometric Study of the Velocity of the Reaction $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{++} + \text{OH}^- \rightarrow [\text{Co}(\text{NH}_3)_5\text{OH}]^{++} + \text{Cl}^-$].

Anal. Assoc. quim., Argentina, vol. 31, 1943, pp. 5-22; British Abs., 1944, p. A-1-252.

For the reaction, the value $k=78\pm1$ at 25°C . was obtained. Special precautions were adopted owing to the rapidity of the reaction.

976. SARKAR, P. B., AND PRASAD, TARA BARAT. [Hexamine Cobaltic Sulfate.] Jour. Indian Chem. Soc., vol. 7, 1930, pp. 119-124; Chem. Abs., vol. 24, 1940, p. 3191².

977. SPACU, G., AND POP, A. [New Class of Ammines, Complex Thioarsenates.] Bull. sec. sci. acad. roumaine, vol. 19, 1937-1938, pp. 117-131 (see Chem. Abs., vol. 32, 1938, p. 72²; and vol. 34, 1940, p. 1582³); Chem. Abs., vol. 34, 1940, p. 5774².

978. SPACU, G., AND VOICHESCU, P. [Higher Ammoniates of Complex Salts.] Ztschr. anorg. allgem. Chem., vol. 243, 1940, pp. 288-296 (see Chem. Abs., vol. 30, 1936, p. 5899²; and vol. 31, 1937, p. 7780²); Chem. Abs., vol. 34, 1940, p. 5012¹.

979. SPACU, PIERRE. [The Aquatization and Hydrolysis of Chloro and Aquo-Pentammine Chlorides [of Cobalt].] Bull. soc. chim. (5), vol. 4, 1937, pp. 130-132 (see Lamb and Marden, Chem. Abs., vol. 6, 1912, p. 567); Chem. Abs., vol. 31, 1937, p. 2541².

The red product obtained by the action of concentrated HCl upon a slightly ammoniacal solution of the chloride and of chloropentammine cobalt is identical (x-ray) with that prepared by Jorgensen (Jour. prakt. chem. (2), vol. 31, 1954, p. 1885). The purpureo salt may be hydrated to form the roseo salt. This, upon heating in strongly ammoniacal solution followed by alcoholic addition, yields a red-violet derivative analogous to the hydroxo derivative prepared by Morgan and Smith (Chem. Abs., vol. 16, 1922, p. 1366). Heating hydroxopentammine cobaltic chloride with HCl yields a bluish red product identical (x-ray) with the purpureo chloride.

980. TRONEV, V. G., BONDIN, S. M., AND KRENOVA, A. L. [Equilibria in Solutions of Cobalt and Nickel Ammoniates at Elevated Temperature and Pressure.] Izvest. Sektora Platiny i Drugikh. Blagorod. Metal Inst. Obschei i. Neorg. Khim. Akad. Nauk, S. S. S. R., No. 23, 1949, pp. 116-122 (see Chem. Abs., vol. 45, 1951, p. 55b, d); Chem. Abs., vol. 45, 1951, p. 2808b.

981. WORMSER, YVETTE. [Notes on the Theory of Reversible Step Reactions of J. Bjerrum, Sorbonne, Paris.] Bull. soc. chim., France, 1954, pp. 387-392; Chem. Abs., vol. 48, 1954, p. 8635c.

A critical discussion is presented on the method of Bjerrum's "function of formation" (Chem. Abs., vol. 35, 1941, p. 6527²). The systems Ag-NH_3 , Hg-NH_3 , Zn-NH_3 , Ni-NH_3 , Co-NH_3 , Ni-en , and Co-en are used to evaluate this method. From the formulas and calculation of equilibrium constants of complexes formed, it is concluded that the hypothesis of reversible step reactions is not convincingly verified. To determine the effective progress of reactions in the formation of complexes, it is suggested that the results obtained by the law of mass action be compared with those obtained by other methods.

CARBONATES

982. CARRIEL, J. T., AND SINGLEY, W. J., JR. (Mellon Institute, Pittsburgh, Pa.). Composition of Basic Nickel Carbonates. Jour. Am. Chem. Soc., vol. 76, 1954, pp. 1389-1343; Chem. Abs., vol. 48, 1954, p. 12599d.

By addition at constant pH and room temperature of standard NiCl_2 and KOH solutions to a solution containing a 10-fold excess of K_2CO_3 , basic Ni carbonates were formed. It was found that in the pH range 8 to

10, the composition changes from $\text{Ni(OH)}_2 \cdot 4\text{NiCO}_3$ to $\text{Ni(OH)}_2 \cdot 3\text{NiCO}_3$, and above pH 10.5, the composition of pure Ni(OH)_2 is approached. There is almost no chloride adsorption by the precipitate. The method of precipitation at constant pH was used to facilitate direct calculation of the composition.

983. CLOUTIER, L., PELLETIER, P. E., AND GAGNON, P. E. The Study of the Precipitation of Carbonates. Trans. Roy. Soc. Canada, vol. 33, III, 1936, pp. 149-164; Chem. Abs., vol. 31, 1937, p. 1315².

When solutions apt to give rise to basic compounds react, mixtures are often obtained, and their composition depends somewhat on the manner of precipitation. A study was made of the precipitation of carbonates of Zn, Cu, Cd, Mg, Co, and Ni. Wet precipitates hydrolyzed normal cobalt carbonates to basic carbonates, the basicity increasing with the concentration of K_2CO_3 . The only definite compound obtained with nickel salts was of the composition $2\text{NiCO}_3 \cdot 5\text{Ni(OH)}_2$.

984. FERRARI, ADOLFO, AND COLLA, C. [The Crystalline Structure of the Neutral Carbonates of Cobalt and Nickel.] Atti. accad. Lincei, vol. 10, 1929, pp. 594-599; Chem. Abs., vol. 24, 1930, p. 2351.

In crystal structure, CoCO_3 is similar to "calcite" and its crystallographic dimensions are $a=5.91\pm0.005$ A. U. $\alpha=103^\circ 22'$ $d=4.24$. The authors were unable to prepare neutral NiCO_3 .

985. KRUSTINSONS, J. [Preparation of Normal Nickel Carbonate According to Senarmont and the Formation of Solid Solutions of Nickel Chloride in Nickel Carbonate.] Ztschr. anorg. allgem. Chem., vol. 212, 1933, pp. 45-48; Chem. Abs., vol. 27, 1933, p. 3891.

Preparation of NiCO_3 by heating a solution of NiCl_2 and CaCO_3 at 160°C . (Senarmont, Ann. chim. phys. (3), vol. 30, 1850, p. 138), gives $m\text{NiCl}_2 \cdot n\text{NiCO}_3$, in which the ratios of m and n vary from 1:2.11 to 1:2.97. This is a solid solution of NiCl_2 in NiCO_3 and shows no spectrum of NiCl_2 . The more concentrated the NiCl_2 solution, the greater the chlorine concentration in the final product. Pure CoCO_3 may be prepared in a similar manner.

986. ROSSETTI-FRANCOIS, J., AND IMELIK, B. (Sorbonne, Paris). [Structure and Constitution of Basic Nickel Carbonates.] Jour. chim. phys., vol. 51, 1954, pp. 451-460; Chem. Abs., vol. 49, 1955, p. 4434d.

Potassium carbonate (330 gm. per l.) was added dropwise to $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (200 gm. per l.), the precipitate washed with distilled H_2O , and the surface area determined by N_2 adsorption at low temperatures. After 15 days washing, the area increased to a maximum of 250 m^2 per gm. At this point, x-ray diffraction indicated a well-crystallized compound, $\text{NiCO}_3 \cdot \text{Ni(OH)}_2$. Rapid heating of this to 200°C . gave an oxide with a surface area of 305 m^2 per gm.

HALIDES

987. CAGLIOTI, V., AND GIACOMELLO, G. [Structural Analysis and Chemical Bonds. V. The Structure of Molecular Lattices Determined by the Fourier Method of Analysis.] Gazz. chim. ital., vol. 69, 1939, pp. 245-254 (see preceding Abs.); Chem. Abs., vol. 34, 1940, p. 296².

The present work is concerned with the molecular lattice of the cholein complex (I) formed from desoxycholic acid (II) and palmitic acid (III) and with related inorganic complexes. When once formed, the (III) lattice can be readily replaced by a compound of similar constitution or of differing chemical constitution but with filiform molecules. Structures of this kind, in which a particular compound acts as an enveloping shell, are known in inorganic chemistry, in which case the elementary cells have vacant positions occupied by various atoms. Various example of such

inorganic coordination are cited, with particular attention to complexes of NH_4Cl and CoCl_2 . Ammonium chloride-cobalt chloride complexes and cholein complexes are analogous in that in each instance, the intermolecular forces differ from the intramolecular forces. In anomalous mixed crystals, NH_4Cl is bound to the other salt by forces different from those that characterize the two.

988. CHATELET, MARCEL. [Oxidation of Cobalt in Ammoniacal Solution.] *Compt. rend.*, vol. 204, 1937, pp. 857-858 (see Chem. Abs., vol. 31, 1937, p. 3366⁶).

Oxygen was passed with agitation into a solution containing CoCl_2 and NH_3 with at least enough NH_4Cl to prevent precipitation. Both velocity and limit of oxidation for a constant concentration of Co depend on the concentration of both NH_3 and NH_4Cl , the initial velocity with constant concentration of NH_4Cl being proportional to the concentration of $[\text{Co}(\text{NH}_3)]^{++}$, by increasing the concentration of which NH_3 affects the velocity of oxidation. The limit of absorption is 1 oxygen molecule per 1 of Co, the valence of which increases from 2 to 4.

989. ———. [System Cobalt (II) Chloride-Ammonium Chloride-Ammonia.] *Jour. chim. phys.*, vol. 38, 1941, pp. 23-29; British Abs., 1947, p. A-210.

Data on the partial precipitation of Co from aqueous CoCl_2 in the presence of varying concentrations of NH_3 and NH_4Cl are given.

990. FEITKNECHT, WALTER. [The Structure of the Basic Salts of Bivalent Metals.] *Helv. chim. acta.*, vol. 16, 1933, pp. 427-454; Chem. Abs., vol. 27, 1933, p. 4147.

991. FEITKNECHT, WALTER, AND COLLET, A. [Basic Salts. XIV. Constitution of Solid Basic Salts of Bivalent Metals. II. Basic Nickel Halides With Simple Laminated Lattices.] *Helv. chim. acta.*, vol. 19, 1936, pp. 831-841; British Chem. Abs., 1936, p. A-1080 (see also p. A-669).

The hydrolysis of aqueous NiCl_2 above 100° C. yields $\text{NiCl}_2 \cdot 3\text{Ni}(\text{OH})_2$ or $\text{NiCl}_2 \cdot \text{Ni}(\text{OH})_2$, according to the concentration. An ill-defined basic bromide, of ideal formula $\text{NiBr}_2 \cdot 3\text{Ni}(\text{OH})_2$, has but a narrow homogeneity range. The lattices of these compounds have been studied by means of x-rays.

992. FEITKNECHT, WALTER, AND FISCHER, G. [Basic Salts. X. Chemistry and Morphology of the Basic Salts of the Cobalt Metals.] *Helv. chim. acta.*, vol. 18, 1935, pp. 555-569 (see Chem. Abs., vol. 29, 1935, p. 4685⁶); Chem. Abs., vol. 29, 1935, p. 5031⁶.

993. ———. [XII. Chemistry and Morphology of Basic Salts of Bivalent Metals. 4. Basic Cobalt Bromide.] *Helv. chim. acta.*, vol. 19, 1936, pp. 448-466 (see Chem. Abs., vol. 29, 1935, pp. 5031⁶ and 7732¹); Chem. Abs., vol. 30, 1936, p. 8056⁶⁻².

At least four basic bromides exist. While their formation may be strongly arrested, once formed, they are very stable and remain metastable over a considerable concentration range.

994. FEITKNECHT, WALTER, AND LOTMAR, W. [The Structure of the Green Basic Cobalt Bromide.] *Ztschr. Krist.*, vol. 91, 1935, pp. 136-141; Chem. Abs., vol. 29, 1935, p. 7732².

995. FERRARI, ADOLFO. [Crystal Structure of Anhydrous Halides of the Bivalent Metals.] *Atti III. congresso naz. chim. pura applicata*, 1930, pp. 452-460; Chem. Abs., vol. 25, 1931, p. 1132⁶.

996. FERRARI, ADOLFO, AND CURTI, RENATO. [Hydroxy Halides of Nickel Obtained by Means of the Senarmont Synthesis.] *Gazz. chim. ital.*, vol. 66, 1936, pp. 104-114; Chem. Abs., vol. 30, 1936, p. 7476⁶.

Experiments confirm the difference in behavior of Ni and Co first described by Ferrari and Colla (Chem.

Abs., vol. 24, 1930, p. 2351), when their halides are heated with CaCO_3 , that is, when aqueous CoCl_2 and CaCO_3 are heated at 150° C. in a sealed tube, CoCO_3 is formed, whereas under the same conditions NiCl_2 and CaCO_3 do not form NiCO_3 . A similar product, identical in x-ray diagram, is formed by heating nickel carbonate with aqueous NiCl_2 for various lengths of time; varying the proportions still produced the same identification as $3\text{Ni}(\text{OH})_2 \cdot \text{NiCl}_2$. Heating for 18 hr. at 230° C. with NiCl_2 yields $\text{Ni}(\text{OH})_2 \cdot \text{NiCl}_2$. Unit cell measurements are given. It is concluded that three hydroxy-chlorides, of the formulas given, exist.

997. FERRARI, ADOLFO, AND GIORGI, F. [The Crystal Structure of Bromides of Bivalent Metals.] *Atti accad. Lincei*, vol. 9, 1929, pp. 1134-1140; Chem. Abs., vol. 24, 1930, p. 1006¹.

998. HIBBERT, DENISE, AND DUVAL, CLEMENT. [Preparation of Cobaltic Chloride.] *Compt. rend.*, vol. 204, 1937, pp. 780-783 (see Chem. Abs., vol. 29, 1935, p. 2872⁷; see also Chem. Abs., vol. 29, 1935, p. 5373⁷); Chem. Abs., vol. 31, 1937, p. 2953⁸.

Cobaltic chloride can be obtained by passing dry Cl_2 over anhydrous CoCl_2 , but the reaction is one of equilibrium and does not proceed to completion. It may also be prepared by electrolysis, with HCl in Et_2O and a Co anode. The salt is a dark-green powder, converted by excess of water to $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ or $[\text{CoCl}(\text{H}_2\text{O})_5]\text{Cl}$. Its transformations and properties are given.

999. JOB, P. [Hydrochloric and Hydrobromic Solutions of the Salts of Cobalt, Copper, and Bivalent Nickel.] *Ann. chim.*, vol. 6, 1936, (XI), pp. 97-144 (see British Chem. Abs., 1935, p. A-582); British Chem. Abs., 1936, p. A-1336.

Solutions of salts of Co, Cu, and Ni in aqueous HCl , HBr , and NaBr have been studied spectrographically. For the Co solution, the adsorption is independent of the anion and proportional to Co^{++} concentration for a fixed concentration of acid. The wave-length and HCl -concentration absorption curves show maxima, while the absorption becomes constant when the HCl concentration exceeds 13 mol. per liter. The results can be accurately reproduced on the assumption that an intermediate complex CoCl^+ and a blue complex CoCl_2 are formed. Hydrobromic acid solutions show similar properties, the blue color appearing, however, at a slightly greater concentration. Solutions of Ni in HBr resemble those of Co and HBr and contain the colored complexes NiBr_2 and NiBr^+ . The equilibrium constants have been calculated in each case and the stabilities of the complexes compared. The intermediate CuBr^+ is more stable than CoBr^+ , while CoBr_2 is less stable than CoCl_2 .

1000. KURNAKOV, N. S., AND EGOROV, V. S. [Dispersion-Type of Solid Solutions in the System $\text{NiCl}_2\text{-NH}_4\text{Cl}\cdot\text{H}_2\text{O}$.] *Bull. acad. sci., U. R. S. S.*, 1936, pp. 547-514. British Chem. Abs., 1937, p. A-I-308.

At 25° and 50° C., the solubility curve consists of 3 parts, 1 of which relates to hydrated NiCl_2 and the two others to 2 series of solid solutions that are found to exist. The composition of the solid phases corresponds throughout with $\text{NiCl}_2\cdot\text{H}_2\text{O}=1:2$. The maximum amount of NiCl_2 in solid solution at 0° C. is 5 percent. At 50° C. in the NH_4Cl -rich solid solution, the NiCl_2 content reaches 24.2 percent, at which value it is in equilibrium with a solid solution of the second series containing 26.8 percent of NiCl_2 . At 50 percent the maximum amount of NiCl_2 present in the second series is 51.2 percent. Examination of the crystals indicates that $\text{NiCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$ does not exist. The second series of solid solutions is produced by dissolution of NH_4Cl in $\text{NiCl}_2 \cdot \text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$, while the first series represents a solution of Ni-carnallite in NH_4Cl .

1001. KUZNETSOV, V. G. [Röntgenographic Investigation of the Anomalous Solid Solutions of Ammonium Chloride Formed in Aqueous Solution With the Chlorides of Manganese, Cobalt, and Nickel.] *Compt. rend. acad. sci., U. R. S. S.*, vol. 15, 1937, pp. 469-471 (in German); *Chem. Abs.*, vol. 31, 1937, p. 8299^a.

Double salts of the type $2\text{NH}_4\text{Cl} \cdot \text{MCl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Co, Mn}$) appear as finely dispersed inclusions in the solid phase when small amounts of MCl_2 are added to NH_4Cl . At 25 to 30 percent MCl_2 the pattern of the double-salt lattice is superposed on the NH_4Cl pattern. At 57 percent (for CoCl_2), the NH_4Cl pattern disappears; and, at 61.1 percent, a new series of weak lines corresponding to $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ present as microscopic inclusions in the solid phase appears. A decrease in the lattice constant of NH_4Cl upon the addition of MCl_2 ($\text{M} = \text{Co, Mn, Ni}$) indicates the formation of solid solutions of the double salt in NH_4Cl .

1002. PAULING, LINUS. The Crystal Structure of the Chlorides of Certain Bivalent Elements. *Proc. Nat. Acad. Sci.*, vol. 15, 1929, pp. 709-712 (*see Chem. Abs.*, vol. 20, 1926, pp. 1344 and 3596); *Chem. Abs.*, vol. 24, 1930, p. 279¹.

1003. VAINSHTEIN, B. K. (Inst. Cryst. Acad. Sci., U. S. S. R., Moscow). [Structure of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ and the Crystallo-Chemistry of Compounds of This Type.] *Zhur. Fiz. Khim.*, vol. 26, 1952, pp. 1774-1784; *Chem. Abs.*, vol. 49, 1955, p. 2147d.

OXIDES AND HYDROXIDES

1004. AZUMA, KIYOSHI, KAMETANI, HIROSHI, AND OKEDA, IWAZO (University of Tokyo). [The Hydrolysis of Salts of Metals in Chlorine Water.] *Jour. Min. Inst., Japan*, vol. 70, 1954, pp. 259-263; *Chem. Abs.*, vol. 48, 1954, p. 13,362i.

The hydrolyses of FeCl_3 , CuCl_2 , CoCl_2 , NiCl_2 , CrCl_3 , and PbO in Cl_2 water were followed by measuring pH and the absorption coefficient ϵ for the wave lengths of the complementary colors to the solutions, the titration being done with 0.1N NaOH . When NaOH is added dropwise to a solution of FeCl_3 in Cl_2 water, pH gradually increases, owing to neutralization of HCl (formed by hydrolysis of Cl_2), and the hydrolysis of FeCl_3 begins to occur at pH 1.5, with the intensified yellow color and at the same time ϵ (at 430 millimicrons) rises steeply (Tyndall effect accompanied). The color then changes to red, ϵ reaches a sharp maximum (pH 5.2) and then decreases to a stationary value. The coagulation of precipitate occurs at maximum ϵ . The isoelectric point of $\text{Fe}(\text{OH})_3$ is pH 5.2 (A. Krause, *Chem. Abs.*, vol. 22, 1928, p. 4075). The compounds CrCl_3 , CoCl_2 , and NiCl_2 give corresponding hydroxides in HCl solutions, but CrCl_3 gives no precipitate in Cl_2 water. Cobaltous chloride and NiCl_2 give the black trivalent hydroxides.

1005. BAGNO, O., AND LONGUET-ESCARD, J. [Irreversible Crystal Growth, Physicochemical Factors and the Growth of Microcrystalline Nickel Hydroxide.] *Jour. chim. phys.*, vol. 51, 1954, pp. 434-438; discussion, pp. 438 and 439, (*see Chem. Abs.*, vol. 45, 1951, p. 7457h); *Chem. Abs.*, vol. 49, 1955, p. 5003b.

The precipitation of $\text{Ni}(\text{OH})_2$ by the addition of 2N NaOH or Na_2CO_3 to 0.2N $\text{Ni}(\text{NO}_3)_2$ or NiCl_2 was investigated. The precipitate initially contains an excess of Ni^{++} ions, adsorbed on the surface of the crystal seeds; this positive charge is compensated for by the adsorption of anions. The double layer of adsorbed ions plays the dominant role in the growth of crystals of $\text{Ni}(\text{OH})_2$, which proceeds by fusion of the crystal seeds and desorption of the adsorbed ions.

1006. BENNETT, O. G., CAIRNS, R. W., AND OTT, EMIL. Crystal Structure of Nickel Oxides. *Jour. Am.*

Chem. Soc., vol. 53, 1931, pp. 1179-1180; *Chem. Abs.*, vol. 25, 1931, p. 2036.

Nickelous oxide prepared by oxidation of $\text{Ni}(\text{OH})_2$ with Cl_2 in alkaline solution and heated to 285° C., corresponds to the previously reported structure for NiO , as it is face-centered cubic. If the NiO is not heated above 110° C., the compound is cubic, but the edge of the unit cube is 4.64 Å. U.; the density is 4.8 as compared to 6.69 for ordinary NiO ; the number of molecules in the unit cell is calculated as 4. Consideration of the intensities of reflection excludes the face-centered cubic type. There is evidence of further modifications.

1007. BESSON, J. [Potentiometric Study of the Oxidation of Nickel, Cobalt, and Manganous Hydroxides.] *Compt. rend.*, vol. 223, 1946, pp. 288-290; *British Abs.*, 1947, p. A-1-92.

1008. ———. [Wet Oxidation of Nickelous, Cobaltous, Manganous, and Ferrous Hydroxides.] *Ann. chim.*, vol. 2, 1947 (XII), pp. 527-598; *British Abs.*, 1948, p. A-1-187.

1009. CAIRNS, R. W., AND OTT, EMIL. X-ray Studies of the System: Nickel-Oxygen-Water. I. Nickelous Oxide and Hydroxide. *Jour. Am. Chem. Soc.*, vol. 55, 1933, pp. 527-533; *Chem. Abs.*, vol. 27, 1933, p. 1795.

Several new modifications of NiO reported in the literature are identical. The lattice parameter of pure NiO is given as $A_0 = 4.1684 \pm 0.0001$ Å. U. The lattice parameters for hexagonal $\text{Ni}(\text{OH})_2$ are given with improved accuracy as $A_0 = 3.114 \pm 0.005$ Å. U. and $C_0 = 4.167 \pm 0.005$ Å. U. The 2 crystal forms of NiSO_4 , previously thought to represent 2 different modifications, are identical. The existence of previously reported hydrates of $\text{Ni}(\text{OH})_2$ is disproved.

II. Compounds Containing Trivalent Nickel, pp. 534-544. X-ray diagrams for the compounds $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{Ni}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ are given. These are not true hydrates, but the H_2O is bound as hydroxyl groups. Structural formulas and x-ray diagrams are given for two compounds of Ni , O , and H_2O at lower stages of oxidation.

1010. DOBROKHOTOV, G. N. [The Magnitude of pH in the Precipitation Process of Metal Hydroxides From Sulfuric Acid Solutions.] *Zhur. Priklad. Khim.*, vol. 27, 1954, pp. 1056-1066; *Chem. Abs.*, vol. 49, 1955, p. 5083c.

1011. DUVAL, C. [Cobalt Hydroxides.] *Compt. rend.*, vol. 205, 1937, pp. 665-668; *British Chem. Abs.*, 1938, p. A-1-156.

The action of aqueous KOH on an aqueous solution of a Co^{3+} salt gives six substances designated alpha garnierite, beta, gamma, delta, epsilon, and zeta.

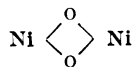
1012. GLEMSER, O., AND EINERHAND, J. [Higher Nickel Hydroxides.] *Ztschr. anorg. Chem.*, vol. 261, 1950, pp. 26-42; *British Abs.*, 1950, p. A-1-644.

Colorimetric titration of strongly alkaline $\text{K}_2\text{S}_2\text{O}_8$ with $\text{Ni}(\text{NO}_3)_2$ takes place in three stages corresponding approximately with the formation of hydrated NiO_2 , Ni_2O_3 , and Ni_3O_4 ; these formulas are confirmed by the oxidizing powers of the precipitates. The primary product of the oxidation is $\text{NiO}_2 \cdot x\text{H}_2\text{O}$, from which the other two hydrated oxides are obtained by further reaction with $\text{Ni}(\text{OH})_2$. Methods of formation, color, existence temperature, and further deductions from x-ray patterns are given.

1013. GORALEVICH, D. K. [Higher Oxygen Compounds of the Eighth Group of the Periodic Table. The Chemical Nature and Structure of Nickel Hydroxides.] *Jour. Gen. Chem., U. S. S. R.*, vol. 1931, pp. 973-990 (*see Chem. Abs.* vol. 25, 1931, p. 2931); *Chem. Abs.*, vol. 26, 1932, p. 4763.

By oxidation of $\text{Ni}(\text{OH})_2$ in NaOH solution with Cl_2 or Br_2 , there are obtained $\text{H}_2\text{Ni}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ (I),

$\text{H}_2\text{Ni}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, $\text{H}_2\text{Ni}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ and $\text{H}_2\text{Ni}_2\text{O}_3 \cdot n\text{HO}_2$. The lower the temperature of oxidation, the greater the number of molecules of water of crystallization that are present. When such compounds are heated, H_2O of crystallization is lost at 105° – 110° C., constitutional water at 130° – 140° C., O_2 from quadrivalent Ni at 140° – 150° C., and O_2 from trivalent Ni at 130° – 140° C. The latter also loses O_2 on heating with acids, and quadrivalent Ni loses O_2 on heating with acids or water. On the basis of these facts, the structure $(\text{HO})_2$



is assigned to (I). The tendency for Ni to replace H atoms in $\text{Ni}(\text{OH})_2$ is general. Similar structural formulas are given to the other compounds obtained. To determine whether other similar elements can behave like Ni, mixtures of different proportions of $\text{Fe}(\text{OH})_2$ and $\text{Ni}(\text{OH})_2$ were oxidized as above. $\text{Fe}_2(\text{H}_2\text{NiO}_4)_3 \cdot 2\text{H}_2\text{O}$, $(\text{FeNi}_2\text{O}_6)_3 \cdot 2\text{H}_2\text{O}$, $\text{Fe}_3(\text{NiO}_4)_3 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_4(\text{Ni}_2\text{O}_6)_3 \cdot 3\text{H}_2\text{O}$ were thus obtained. By reasoning along the above lines, structural formulas are given for these compounds.

1014. HACKSPILL, L., AND KIEFFER, A. P. [Hydrates of Oxides and of Mineral Salts.] *Ann. chim.* (10), vol. 14, 1930, pp. 227–282; *Chem. Abs.*, vol. 25, 1931, p. 260².

At ordinary temperatures in vacuo, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ loses 5 H_2O . The remaining 2 H_2O are removed slowly between ordinary temperature and 320° C. and are H_2O of semiconstitution. Nickelous sulfate heptahydrate behaves very much as the Co salt.

1015. HÜTTIG, G. F., AND KASSLER, ROBERT. [Study of Oxide Hydrates. XXI. The System Cobaltous Oxide-Water.] *Ztschr. anorg. allgem. Chem.* vol. 187, 1930, pp. 16–23; *Chem. Abs.*, vol. 24, 1930, p. 2076².

Four hydrated oxides were prepared: (A₁) $\text{CoO} \cdot 1.85\text{H}_2\text{O}$, (A₂) $\text{CoO} \cdot 0.02 \text{ Co}_2\text{O}_3 \cdot 0.73 \text{ H}_2\text{O}$, (B₁) $\text{CoO} \cdot 1.941 \text{ H}_2\text{O}$, and (B₂) $\text{CoO} \cdot 0.017 \text{ Co}_2\text{O}_3 \cdot 0.91 \text{ H}_2\text{O}$. They are first subjected to isobaric dehydration (10 mm.), a sharp break occurring at the point $\text{CoO} \cdot 1\text{H}_2\text{O}$ with a temperature of 168° C. Debye diagrams show interference lines in the same positions for A₁ and B₁; the A₁ lines, however, are somewhat weaker and less sharply defined. The dehydration curve of A₁ shows that about 1.5 molecules of water are more strongly bound than mechanically held H_2O could be. Two phases must be present in the basic substance, a crystalline monohydrate $\text{CoO} \cdot 1\text{H}_2\text{O}$ and a decomposition product with the approximate composition $\text{CoO} \cdot 0.4 \text{ H}_2\text{O}$. The last traces of H_2O are firmly held, some being present at 300° C. Comparison of the Debye diagrams of A₁ and B₁ shows that these preparations have the same crystal lattice, and one that is different from that of H_2O -free CoO . It is concluded that at room temperature and probably also at much lower temperatures, the monohydrate has no stable zone of existence and the decomposition pressure corresponds to no thermodynamic equilibrium.

1016. HÜTTIG, G. F., AND PETER, ALFRED. [Study of Oxide Hydrates. XXIV. The System Nickel^{III} Oxide-Water.] *Ztschr. anorg. allgem. Chem.*, vol. 189, 1930, pp. 183–189; *Chem. Abs.*, vol. 24, 1930, p. 3188.

The compounds studied were combinations of NiO with 1.862, 2.05, and 2.439 molecules of water. The decomposition temperature at $p=10$ mm. was found to be 230° C. The Debye diagrams can be classed into two types, one constituting annealed NiO, and the other the monohydrate.

XXV. The System Nickel^{III} Oxide-Water. Work cited above, pp. 190–195. All of the oxide hydrates studied were combinations of Ni_2O_3 with 3.5, 4.244, 3.38, 0.956, and 3.61 molecules of H_2O . Isobaric

decomposition of 10 mm. is studied, and Debye diagrams were made. The system $\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}$ coincides in important aspects with the system $\text{Co}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and establishes the existence of a monohydrate. At $p=10$ mm. the monohydrate decomposes at 138° C. according to the equation: $2(\text{Ni}_2\text{O}_3 \cdot \text{H}_2\text{O}) \rightarrow 4\text{NiO} + 2\text{H}_2\text{O} + \text{O}_2$. The formation of a nickel oxide hydrate with a higher oxygen content than Ni_2O_3 is considered possible.

1017. KATSURAI, T. [Influence of Autoclave Treatment on the Form of Hydroxides and on the Nature of Colloidal Suspension.] *Sci. Papers, Inst. Phys. Chem. Research, Tokyo*, vol. 12, 1929, pp. 161–166; *Chem. Abs.*, vol. 24, 1930, p. 4686⁵.

When gelatinous $\text{Fe}(\text{OH})_3$ is heated with a slight excess of alkali under a pressure of 5 to 10 atmospheres, a very fine form similar to rouge is obtained. The hydroxides of Mg, Al, Cr, and Co, prepared by adding a slight excess of either NaOH or NH_3 to salts of these metals, suffered no change under this treatment.

1018. KONDRASHEV, Y. D., AND FEDOROVA, N. N. [Crystal Structure of CoHO_2 .] *Doklady Akad. Nauk. S. S. S. R.*, vol. 94, 1954, pp. 229–231; *Chem. Abs.*, vol. 49, 1955, p. 2146c.

1019. LIEVIN, O., AND HERMAN, J. [Auto-Oxidation of the Hydroxides of Iron, Manganese, and Cobalt.] *Compt. rend.*, vol. 200, 1935, pp. 1474–1477; *British Chem. Abs.*, 1935, p. A–834.

An apparatus for measuring the rate of oxidation by O_2 of $\text{Fe}(\text{OH})_2$, $\text{Mn}(\text{OH})_2$, and $\text{Co}(\text{OH})_2$, respectively, suspended in alkaline solution, is described. The oxidation to Fe_2O_3 is very rapid, and appears to follow a simpler course than the other two. $\text{Mn}(\text{OH})_2$ oxidation stops at a stage intermediate between Mn_2O_3 and MnO_2 . The maximum for $\text{Co}(\text{OH})_2$, Co_2O_3 , is attained much more slowly than in the other two cases. The oxidizability of $\text{Co}(\text{OH})_2$ appears to depend on the color of the original precipitate.

1020. LONGUET, J. [Precipitated Nickel Hydroxide.] *Compt. rend.*, vol. 223, 1946, pp. 150–151; *British Abs.*, 1947, p. A–188.

Nickelous hydroxide, precipitated by NaOH or aqueous NH_4OH , when examined by x-ray diffraction, shows, besides the $\text{Ni}(\text{OH})_2$ diagram, fairly intense lines probably due to an oxychloride, $\text{NiCl}_2 \cdot n\text{Ni}(\text{OH})_2$. This may be the cause of anomalies in the diffraction pattern of $\text{Ni}(\text{OH})_2$, reported by Feitknecht (A, 1942, 1–251).

1021. LONGUET-ESCARD, J., AND MERING, J. [Application of the Quantitative Methods of Diffraction to the Study of the Growth of Nickel Hydroxide.] *Jour. chim. phys.*, vol. 51, 1954, pp. 440–445; *Chem. Abs.*, vol. 49, 1955, p. 5062h.

The application of x-ray diffraction methods to the determination of the crystal structure of $\text{Ni}(\text{OH})_2$ is described.

1022. MÜLLER, RICHARD. *Das System Nickeloxyd-Sauerstoff-Wasser* [The System Nickel Oxide, Oxygen, Water]. Leipzig, 1931, 67 pp. Thesis; *Chem. Abs.*, vol. 27, 1933, p. 1267.

1023. NATTA, G., AND STRADA, M. (Reale Politecnico, Milano). [Oxides and Hydroxides of Cobalt.] *Gazz. chim. ital.*, vol. 58, 1928, pp. 419–433; *Chem. Abs.*, vol. 23, 1929, p. 783¹.

The present paper, an amplification of earlier ones (see Natta and Reina, *Chem. Abs.*, vol. 20, 1926, p. 3390; Natta and Schmid, *Chem. Abs.*, vol. 21, 1927, p. 214) is an attempt to determine what oxides of Co really do exist and their crystalline structure and thus to end the confusion that prevails in the literature. Three oxides of definite chemical composition and structure were identified, CoO , Co_3O_4 , and Co_2O_3 . In the hydrox-

ides only $\text{Co}(\text{OH})_2$ has a definite chemical composition and structure. $\text{Co}(\text{OH})_2$ could not be obtained as a substance with definite crystal structure and by x-ray examination showed the same lines as pure Co_2O_3 , which it forms on dehydration.

1024. PARIS, R. [Solubility of Nickel Hydroxide in Aqueous Ammonia as Evidence for the Formation of Basic Nickel-Ammonium Complexes.] *Compt. rend. Acad. sci., Paris*, vol. 232, pp. 840-841; *British Abs.*, 1952, p. A-1-243.

Aqueous solutions of ammonia with strengths of 0.6 to 10.0 N aqueous NH_3 dissolve increasing amounts of $\text{Ni}(\text{OH})_2$, as the (NH_3) increases, and solubility measurements in this concentration range are tabulated. Later experiments indicate that the $\text{Ni}(\text{OH})_2$ solubility reaches a maximum at $(\text{NH}_3) \approx 13\text{N}$ and falls again as (NH_3) is increased further. In solutions more dilute than 3N, the solubility data support the hypothesis that a complex $\text{Ni}(\text{OH})_2 \cdot 2\text{NH}_3$ exists.

1025. SHAW, C. S., AND GHOSH, S. Precipitation of Nickelous Hydroxide Under Different Conditions and Its Solubility in Aqueous Ammonia. *Jour. Indian Chem. Soc.*, vol. 27, 1950, pp. 679-682; *British Abs.*, 1952, p. A-1-119.

Observations are recorded on the solubility of nickelous hydroxide, prepared under various conditions. Less than the theoretical quantity of alkali is needed to precipitate nickelous hydroxide completely from a soluble Ni salt, and less alkali is required in hot solutions than in cold; also the quantity of alkali approaches theoretical in dilute solutions. Using increased alkali, the solubility in aqueous ammonia decreases for the $\text{Ni}(\text{OH})_2$.

1026. SIEGMANN, FRIEDRICH (assigned to Deutsche Gold- und Silber Scheideanstalt vormals Roessler). [Nickel Hydroxide.] *German Patent* 706,449, Apr. 24, 1941 (*Cl. 12n 4*); *Chem. Abs.*, vol. 36, 1942, p. 2096^a.

Nickel hydroxide, swelling only slightly or not at all when in contact with water, is prepared by precipitating the alkali hydroxides in organic liquids, for example, MeOH or EtOH.

1027. SOBOL, S. I. Structure of Precipitates of Cobalt and Nickel Hydroxides. *Jour. Gen. Chem., U. S. S. R.*, vol. 23, 1953, pp. 941-943 (English trans.) (*see Chem. Abs.*, vol. 48, 1954, p. 3109c); *Chem. Abs.*, vol. 49, 1955, p. 5083f.

1028. —. Physicochemical Conditions of Precipitation, Heat of Formation, and Solubility Product of Cobalt Hydroxide. *Jour. Gen. Chem., U. S. S. R.*, vol. 23, 1953, pp. 945-954 (English trans.) (*see Chem. Abs.*, vol. 48, 1954, p. 3109e); *Chem. Abs.*, vol. 49, 1955, p. 5083f.

1029. TSANGARAKIS, C., AND SIBUT-PINOTE, R. [Dehydration of Nickel Hydroxide, the Kinetics, and Evolution of the Structure and Constitution, as Shown by X-Ray Diffraction and Adsorption Measurements.] *Jour. chim. phys.*, vol. 51, 1954, pp. 446-450; *Chem. Abs.*, vol. 49, 1955, p. 5093d.

Nickelous hydroxide precipitated from N NiCl_2 and N NaOH was washed four times in distilled water and dried over H_2SO_4 . Dehydration in a stream of H_2 shows that only 20 percent H_2O is lost after 4 hours at 350°C , reduction setting in at 150°C . Four samples of $\text{Ni}(\text{OH})_2$ were dehydrated at 125°C for 200 hr., 160°C for 600 hr., 250°C for 500 hr., and 300°C for 600 hr. respectively. X-ray diffraction shows a progressive evolution from hexagonal $\text{Ni}(\text{OH})_2$ to cubic NiO . Adsorption of N, at -195°C gave values for the surface areas of 209, 264, 96, and 66 m^2 per gm. respectively.

1030. VAN EIJK VAN VOORTHUIJSEN, J. J. R., AND FRANZEN, P. [Structure and Compounds Formed During the Preparation of Nickel on Silica Cat-

alysts.] *Rec. trav. chim. Pays-Bas*, vol. 70, 1951, pp. 793-812; *British Abs.*, 1952, p. A-1-118.

SULFATES

1031. BEEVERS, C. A., AND LIPSON, H. The Crystal Structure of Nickel Sulfate Hexahydrate, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. *Ztschr. Krist.*, vol. 83, 1932, pp. 123-135 (in English); *Chem. Abs.*, vol. 26, 1932, p. 5467.

1032. BEEVERS, C. A. AND SCHWARTZ, C. M. The Crystal Structure of Nickel Sulfate Heptahydrate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. *Ztschr. Krist.*, vol. 91, 1935, pp. 157-169 (in English); *Chem. Abs.*, vol. 29, 1935, p. 7732^e.

The structure of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (*see Chem. Abs.*, vol. 21, 1927, p. 1384) has SO_4 groups and octahedral groups of $6\text{H}_2\text{O}$ around Ni, and an extra water molecule. The H_2O molecules are of two types, and the coordination group contains both groups exactly as in the lower hydrate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Parameters were determined by a 2-dimensional Fourier analysis.

1033. BENRATH, ALFRED. [Polytherms of the Ternary Systems Which, in Addition to Water, Contain an Alkaline Sulfate and a Vitriol Former.] *Ztschr. anorg. allgem. Chem.*, vol. 208, 1932, pp. 169-176 (*see Chem. Abs.*, vol. 26, 1932, p. 1869); *Chem. Abs.*, vol. 27, 1933, p. 36.

The systems $\text{CoSO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$, $\text{CoSO}_4\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$, $\text{CoSO}_4\text{--Rb}_2\text{SO}_4\text{--H}_2\text{O}$, $\text{NiSO}_4\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$, $\text{NiSO}_4\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$, $\text{NiSO}_4\text{--Tl}_2\text{SO}_4\text{--H}_2\text{O}$, and $\text{NiSO}_4\text{--Rb}_2\text{SO}_4\text{--H}_2\text{O}$ were studied, and solubility polytherms were plotted. The molecular solubility of the double salt decreases with increasing atomic weight of the alkali metal. Increase in the solubility of the double salt with increase in temperature indicates increasing decomposition in its components as the temperature rises.

1034. BENRATH, A., AND THIEMANN, W. [Mixed Crystals in the Vitriol Series.] *Ztschr. anorg. allgem. Chem.*, vol. 217, 1934, pp. 347-352 (*see Chem. Abs.*, vol. 27, 1933, p. 36); *Chem. Abs.*, vol. 28, 1934, p. 4330^a.

The system $\text{NiSO}_4\text{--CoSO}_4\text{--H}_2\text{O}$ was studied from 0° to 98.2°C . Only the isomorphous monohydrates are miscible in all proportions, while the monoclinic heptahydrate of CoSO_4 and the rhombic heptahydrate of NiSO_4 , as well as the tetragonal hexahydrate of NiSO_4 , and the monoclinic hexahydrate of CoSO_4 , are miscible to a limited extent. The point of transformation of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is about 103°C . The transformation of blue $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ to the green salt is at 53.3°C .

1035. CAVEN, R. M., AND GARDNER, W. K. Equilibria in the Systems $(\text{NH}_4)_2\text{SO}_4\text{--NiSO}_4\text{--H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4\text{--CoSO}_4\text{--H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4\text{--ZnSO}_4\text{--H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{--NiSO}_4\text{--H}_2\text{O}$, and $\text{Na}_2\text{SO}_4\text{--CoSO}_4\text{--H}_2\text{O}$ at 25°C . *Jour. Chem. Soc.*, 1933, pp. 943-946 (*see Chem. Abs.*, vol. 22, 1928, p. 4399); *Chem. Abs.*, vol. 27, 1933, p. 5624.

1036. COREY, R. B., AND WYCKOFF, R. W. G. [The Structure of Tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.] *Ztschr. Krist.*, vol. 84, 1933, p. 477; *Chem. Abs.*, vol. 27, 1933, p. 2360.

The structure of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ as determined by Beevers and Lipson (*Chem. Abs.*, vol. 26, 1932, p. 5467) is completely verified.

1037. CROCKFORD, H. D., AND BRAWLEY, D. J. System: Copper Sulfate-Cobalt Sulfate-Water. *Jour. Phys. Chem.*, vol. 36, 1932, pp. 1594-1596; *Chem. Abs.*, vol. 26, 1932, p. 3721.

The 0° and 25°C isotherms for $\text{CuSO}_4\text{--CoSO}_4\text{--H}_2\text{O}$ were determined. At both temperatures, the solids are $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and a series of solid solutions in which the Cu partly replaces Co in $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$.

1038. FEITKNECHT, W., AND FISCHER, G. [Basic Salts. VIII. Basic Cobalt Sulfates. IX. Chemistry and

Morphology of Basic Salts of Bivalent Metals. General.] *Helv. chim. acta*, vol. 18, 1935, pp. 28-40 and 40-60; *Chem. Abs.*, vol. 29, 1935, p. 4685⁹.

The subject is treated from the viewpoints of chemistry, physicochemistry, genetics, and structure. The compound $\text{CoSO}_4 \cdot 3\text{Co}(\text{OH})_2$ crystallizes with difficulty in microscopic hexagonal leaflets, with a lattice of alternate layers of hydroxide and normal salt. The amount of zeolitic water varies but usually is 4 molecules. The blue compound is converted by concentrated aqueous CoSO_4 into a violet basic salt $2\text{CoSO}_4 \cdot 3\text{Co}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, which may be either rhombic or monoclinic. When CoSO_4 is hydrolyzed by urea, basic salts in which the SO_4^{--} is partly replaced by CO_3^{--} are formed.

1039. JOOS, G. [Nature of Hydrate Binding for the Ions of the Transition Elements, Particularly Co.] *Ann. Physik.*, V, vol. 28, 1937, pp. 54-58; *British Chem. Abs.*, 1937, p. A-I-66.

The compound $\text{Co}_2(\text{SO}_4)_3 \cdot \text{Rb}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ shows a very weak paramagnetic susceptibility (χ) determined by the weighing method in a nonhomogeneous field. χ varies with temperature in the normal way. In this compound, hydrate formation of the Co^{+++} ion is brought about by a rebuilding of the electron shell with true complex formation. The complex is however, much less stable than $[\text{Co}(\text{NH}_3)_6]^{+++}$. For all other ions of the Fe group, the H_2O is bound by electrostatic forces.

1040. SIMON, A., AND KNAUER, K. [The Hydrates of Cobalt, Nickel, and Copper Sulfates.] *Ztschr. anorg. allgem. Chem.*, vol. 242, 1939, pp. 375-392; *Chem. Abs.*, vol. 34, 1940, p. 1268⁹.

Dehydration and tensimetric measurements on $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ indicate the existence of $\text{CoSO}_4 \cdot 6.5\text{H}_2\text{O}$ at 18° C. and $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ at 29.5° C. The salt $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ can be converted to tetragonal $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. Treatment of the hexahydrates with anhydrous liquid NH_3 indicates that 1 molecule of H_2O is bound in a different manner from the others. Ni and Co form the hexamine monohydrate. Tensimetric decomposition of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ at 11 mm. pressure indicates $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 4\text{H}_2\text{O}$.

1041. TAO, L. O., AND MO, W. S. [Equilibria Between the Aquoammino-Cobaltic Sulfates and Their Sulfuric Acid Solution at 45° C.] *Bull. Soc. chim.*, France, vol. 2, 1935, pp. 911-916 (see *British Abs.*, 1929, p. A-1409); *British Chem. Abs.*, 1935, p. A-824.

1042. ———. [Equilibrium Between the Sulfates of Cobaltic Chloropentammine and Their Sulfuric Acid Solutions.] *Compt. rend.*, vol. 202, 1936, pp. 846-848; *British Chem. Abs.*, 1936, p. A-564.

OTHER MATERIALS

1043. BABKO, A. K., AND KOROTUN, M. V. (State University, Kiev). [Complex Formation Between Bivalent Cobalt and Dimethylglyoxime.] *Zhur. Obshch. Khim.*, vol. 24, 1954, pp. 597-605 (see preceding abstract (on copper)); *Chem. Abs.*, vol. 49, 1955, p. 2928e.

Cobaltous chloride and dimethylglyoxime in Me_2CO in the presence of air gave a compound of trivalent Co that has been written $[\text{Co}(\text{H}_2\text{Dm})_2]\text{Cl}$. Best yields result when the mixture is not heated.

1044. BANKS, W. H., RIGHELLATO, E. C., AND DAVIES, C. W. The Extent of Dissociation of Salts in Water. *Trans. Faraday Soc.*, vol. 27, 1931, pp. 621-627 (see work cited above, vol. 23, 1927, pp. 351-356; *Chem. Abs.*, vol. 25, 1931, p. 1720); *Chem. Abs.*, vol. 26, 1932, p. 20.

The calculations of dissociation from conductivity data were extended to CsNO_3 , NaClO_4 , NaBrO_3 ,

$(\text{NH}_4)_2\text{SO}_4$, $\text{Ba}(\text{BrO}_3)_2$, K_2CrO_4 , $\text{K}_2\text{C}_2\text{O}_4$, and the chlorides and nitrates of Zn, Cu, Ni, Co, Mn, and Ca. The univalent salts show great deviations from the requirements of the Debye-Hückel theory.

1045. BERNARD, R., AND JOB, P. [The Oxidation of Salts of Cobalt in Alkaline Solution.] *Compt. rend.*, vol. 190, 1930, pp. 186-187; *Chem. Abs.*, vol. 24, 1930, p. 2960¹.

Salts of Co in concentrated solutions of the alkali carbonates are pink but upon oxidation acquire an intense green coloration. The absorption of various mixtures was measured and from the results, it is concluded that the passage from the bivalent to the trivalent state of Co is accompanied by the formation of an intermediate compound in which Co is quadrivalent.

1046. BHATTACHARYA, G. C., AND SINHA, P. C. (Science College, Patna). [Quinoline Complexes of Thiocyanates of Zinc, Cadmium, Nickel, and Cobalt.] *Jour. Indian Chem. Soc.*, vol. 30, 1953, pp. 714-716; *Chem. Abs.*, vol. 48, 1954, p. 10,473h.

The preparation, properties, and stability of the quinoline complexes of the thiocyanates of Zn, Cd, Ni, and Co are discussed.

1047. BURGERS, W. G., AND BASART, J. C. M. [Lattice Constants of Mixed Crystals of Copper-Nickel.] *Ztsch. Krist.*, vol. 75, 1930, pp. 155-157; *Chem. Abs.*, vol. 25, 1931, p. 1421¹.

1048. CLARK, H. C., AND ODELL, A. L. (Auckland University College, New Zealand). The Properties of Some Nickel Complexes in Solution. *Chem. and Ind.*, 1954, pp. 1510-1511; *Chem. Abs.*, vol. 49, 1955, p. 6763d.

Magnetic susceptibilities of solutions of Ni chelates formed with salicylaldehyde derivatives show that the solvents used influence the type of magnetism displayed. Pyridine, alcohol, and dioxan apparently solvate the complex molecules to form compounds that are octahedral in structure and contain two solvent molecules per Ni atom. In chloroform, benzene, toluene, and xylene solutions the equilibria appear to be between planar diamagnetic and tetrahedral paramagnetic forms.

1049. DÖNGES, E. [Chemistry of Cobalt and Nickel Sulfides.] *Ztschr. Naturforsch.*, vol. 1, 1946, pp. 221-222; *British Abs.*, 1948, p. A-I-90.

Sulfides precipitated by Na_2S or $(\text{NH}_4)_2\text{S}$ from solutions of Co and Ni salts are readily oxidized in air to give SCoOH and SNI OH . By the action of acid, parts of the precipitate are dissolved to give dibasic Co or Ni salts. S is precipitated. The remainder of the precipitate is rendered insoluble by the action of excess S. The solubility in mineral acids of precipitated cobalt and nickel sulfides depends on the method of preparation. Various cases are discussed. Damp SCoOH and SNI OH oxidize Co to CO_2 at room temperature and catalyze the oxidation of CO by air. Also, in the presence of damp SCoOH and SNI OH , S reacts with CO at room temperature $\text{S} + \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{S} + \text{CO}_2$. Cubic Co_3S_4 is precipitated, together with CoS , by the action of H_2S on solutions of Co salts containing a low concentration of mineral acid.

1050. EHRLIG, HILDEGARD. [The Reaction of Metals Toward Salts, in Particular Toward Ammonium Salts in the Presence or Absence of Ammonia.] *Ztschr. anorg. allgem. Chem.*, vol. 206, 1932, pp. 385-397; *Chem. Abs.*, vol. 26, 1932, p. 5508.

The object of the investigation was to find the causes of the dissolution of metals after electrolytic deposition from ammoniacal solutions. The metals tested were Cu, Bi, Pb, Ni, Co, Fe, Ca, Zn, and Mg in solutions of NH_4OH , and of NH_4NO_3 , NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, NaNO_3 , and KNO_3 with and without NH_3 . Cd, Zn, and Mg are strongly affected, Cu less so, unless

exposed to the air. Cd reduces NH_4NO_3 to NH_4NO_2 . Zn and Mg evolve N_2O with NH_4NO_3 , as a result of the reaction of the products NH_4NO_2 and NH_4OH . The solution of Cd cannot be completely stopped by passing a current of electricity through it. NaNO_3 has much less solvent action than NH_4NO_3 . Ammonium nitrate solution has a strong solvent action on Mg and Cd, less so on Zn. Addition of NH_3 increases the effect strongly on Zn, slightly on Cd, but reduces it on Mg. This effect is due to solubility of the hydroxides of these metals in NH_4NO_3 solution. In the case of Zn, NH_3 helps to dissolve the hydroxide to complex salts.

1051. FEIGL, FRITZ, DEMANT, VIKTOR, AND DE OLIVEIRA, O. E. [Hydrogen Cyanonickelate and Its Salts.] *Anais assoc. quim. Brasil*, vol. 3, 1945, pp. 72-87; *Chem. Abs.*, vol. 39, 1945, p. 3219³.

1052. FEITKNECHT, W., AND FISCHER, G. [Basic Salts. XV. Chemistry and Morphology of Basic Salts of Bivalent Metals. V. Basic Cobalt Nitrates.] *Helv. chim. acta*, vol. 19, 1936, pp. 1242-1255; *British Chem. Abs.*, 1937, p. A-1-95.

1053. FERSMAN, A. E. [Bivalent Cobalt.] *Bull. acad. sci. U. R. S. S.*, Ser. geol., No. 3, 1939, pp. 7-22 (in English, p. 23); *Chem. Abs.*, vol. 34, 1940, p. 3197⁶.

Bivalent Co has in certain cases, for example, in sulfides and some of the oxides, a coordination number of 4. Such compounds have a semimetallic or metallic character as compared to the ion-type Co salts with the usual coordination number 6. The variable coordination number distinguishes Co from Fe and Ni and appears to be the key to the geochemistry of this element, that is, the frequency of its occurrence in the earth's crust and the type of Co minerals found. Deposits of Co in Russia are listed, and its uses as a pigment, as a catalyst, an alloying component, and a biological agent are reviewed (20 refs.).

1054. FIALA, SILVIO. Oxygenation and Its Models. Chelates. *Biol. Listy*, vol. 28, 1947, pp. 201-208 (English summary); *Chem. Abs.*, vol. 48, 1954, p. 7655g.

A description of oxygenation models prepared by Tsumaki, Calvin, and others (*Chem. Abs.*, vol. 41, 1947, p. 656e) and Burk (*Chem. Abs.*, vol. 41, 1947, p. 1337a) in the form of various chelate complexes of Co^{++} is presented.

1055. FUJII, SABURO, AND SUMITANI, MITUKUNI (Tokyo Institute of Technology). [Reversible Change Between the Planar and Tetrahedral Configurations in Some Nickel Complexes in Solution.] *F. Ishikawa anniversary vol.*, *Sci. Repts.*, Tōhoku Univ., vol. 37, No. 1, 1953, pp. 49-54; *Chem. Abs.*, vol. 49, 1955, p. 31e.

1056. FYLKING, K. E. [Phosphides and Arsenides With Modified Nickel Arsenide Structure.] *Arkiv. Kemi. Min. Geol.*, vol. 11, B, No. 18, 1935, 6 pp.; *British Chem. Abs.*, 1935, p. A-920.

Mn, Fe, and Co phosphides and arsenides, prepared by heating the elements in equal molecular proportions for not less than a day at 610°C . (for P) or 730°C . (for As) have lattice structures closely related to that of NiAs, but the metal atoms form zigzag chains instead of straight rows. Manganese arsenide differs less from NiAs than FeAs and CoAs. The lattice dimensions of these compounds and parameter values for MnP and FeAs are recorded.

1057. GOLDSCHMIDT, V. M. (Oslo University). [Atomic Distances in Metals.] *Ztschr. physik. Chem.*, vol. 133, 1928, pp. 397-419; *Chem. Abs.*, vol. 23, 1929, p. 1787⁸.

The atomic radii of groups of metals are reported, with theory of coordination numbers. There is a definite relation between the coordination number and the atomic distance. For the series Mn, Fe, Co, Ni,

Cu, Zn, and Ge the respective dimensions are 1.36, 1.27, 1.257, 1.244, 1.276, 1.374, and 1.39 A. U.

1058. HAWLEY, J. E., AND HEWITT, D. F. Pseudo-Eutectic and Pseudo-Ex-Solution Intergrowths of Nickel Arsenides Due to Heat Effects. *Econ. Geol.*, vol. 43, No. 4, June-July 1948, pp. 273-279; *Eng. Index*, 1948, p. 832.

Pseudo-eutectic and pseudo-ex-solution intergrowths are described and compared with natural intergrowth of these minerals. The suggestion is made that similar natural intergrowths of both maucherite in niccolite and of some pentlandite in pyrrhotite may be due primarily to the heat effect of later invading ore solutions, or to decrease in containing pressures while ores are still at elevated temperatures.

1059. HEWITT, D. F. Partial Study of NiAs-NiSb System by X-ray Analysis. *Econ. Geol.*, vol. 43, No. 5, August 1948, pp. 408-417; *Eng. Index*, 1948, p. 832.

Artificial niccolite and breithauptite were synthesized. Thermal studies of NiAs-NiSb system show that nickel arsenide and nickel antimonide form complete solid solution series in one another.

1060. JAFFRAY, JEAN, AND RODIER, NŒL. [Transitions in Crystals of Nickel Nitrate Hexahydrate.] *Compt. rend.*, vol. 238, 1954, pp. 1975-1977; *Chem. Abs.*, vol. 48, 1954, p. 13,393f.

By means of thermal analysis and dilatometry, 5 transitions are observed at the following temperatures in $^\circ\text{K}$: 150° , 169° , 205.5° , 238° , and 259° .

1061. MAZZA, L., AND NASINI, A. G. The Crystal Structure of Nickel. *Phil. Mag.* (7), vol. 7, 1929, pp. 301-311; *Chem. Abs.*, vol. 23, 1929, p. 2620¹.

Dimensions of crystal particles range from 10^{-2} to 10^5 cm., with the elementary cell edge at about 3.514 A. U. Changes in the structure with various treatments and at various temperatures are discussed.

1062. MCALPINE, R. K. Anomalous Behavior of Some Oxidizing Agents. *Jour. Chem. Educ.*, vol. 23, 1946, pp. 301-305; *British Abs.*, 1947, p. A-I-153.

Attention is directed to several cases in which there is little connection between the "strength" of NaOCl , H_2O_2 , and $\text{K}_2\text{S}_2\text{O}_8$ as oxidizing agents and the readiness with which they carry out particular oxidations, or between the "strength" of Mn^{++} , $\text{Co}(\text{NH}_3)_6^{++}$, $\text{Ni}(\text{OH})_2$, NH_3 , and N_2H_4 as reducing agents, and the readiness with which they can effect specific reductions.

1063. NAST, R., AND KRAKKAY, T. V. (Technische Hochschule, Munich, Germany). [A Potassium Cyanonickelate.] *Ztschr. Naturforsch.*, vol. 9b, 1954, pp. 798-799 (see Maletesta and Pizzotti, *Chem. Abs.*, vol. 37, 1943, p. 5919⁹); *Chem. Abs.*, vol. 49, 1955, p. 10,112d.

The preparation of $\text{K}_2[\text{Ni}(\text{CN})_6]$, by reduction with $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ of a suspension of anhydrous $\text{Ni}(\text{CN})_2$, in a strongly alkaline solution of $\text{K}_2[\text{Ni}(\text{CN})_6]$, did not yield an analytically pure product unless the molecular ratio of $\text{Ni}(\text{CN})_2$ to $\text{K}_2[\text{Ni}(\text{CN})_6]$ was 1 : 1.

1064. NATTA, G., AND PASSERINI, L. [Thio Salts Having the Spinel Structure.] *Atti. accad. Lincei*, vol. 14, 1931, pp. 33-37 (see *Chem. Abs.*, vol. 24, 1930, p. 1311, and vol. 25, 1931, p. 2892); *Chem. Abs.*, vol. 26, 1932, p. 1868.

The structure of several linneites, for example, Co_3S_4 , Ni_3S_4 , have been studied; these have the spinel structure with a cubic lattice with a side 9.41 ± 0.01 A. U. in all the samples studied.

1065. NOYES, A. A., AND DEAHL, T. J. Strong Oxidizing Agents in Nitric Acid Solution. III. Oxidation Potential of Cobaltous-Cobaltic Salts: Kinetics of the Reduction of Cobaltic Salts by Water. *Jour. Am. Chem. Soc.*, vol. 59, 1937, pp. 1337-1344 (see *British*

Chem. Abs., 1936, p. A-1072); British Chem. Abs., 1937, p. A-1-465.

From e. m. f. measurements the formal oxidation potential for Co^{III} to Co^{II} is calculated to range from 1.800 volts in 1f- HNO_3 to 1.816 volts in 4f- HNO_3 at 0° C. and from 1.842 volts in 3f- HNO_3 to 1.850 volts in 4f- HNO_3 at 25° C. The decrease in free energy and heat content has also been calculated.

1066. PRIYADARANJAN, RAY, AND DWIJENDRA, N. S. V. Valency of Nickel and Nature of the Bond in Arsenical Nickel Ores. Jour. Indian Chem. Soc., vol. 25, 1948, pp. 205-208 (see preceding Chem. Abs.); Chem. Abs., vol. 43, 1949, p. 4167g.

Magnetic susceptibilities of specimens of nickel-sulfur arsenide ($1.85_{\text{mu}} \text{u}$) and nickel arsenide ($0.72_{\text{mu}} \text{u}$) showed that in the former the Ni atom is in an oxidation state of 3 and is covalently bound to ars nic in an octahedral configuration, while in the latter the bonds are metallic in character. These conclusions agree with interatomic distances and crystal structure determined by the x-ray method.

1067. SCHMID, GERHARD, AND EHRET, LOTHAR. [The Effect of Ultrasound on the Passivity of Metal.] Ztschr. Electrochem., vol. 43, 1937, pp. 408-415 (see Chem. Abs., vol. 30, 1936, p. 3287⁵); Chem. Abs., vol. 31, 1937, p. 7315⁷.

Several examples of the effect of ultrasonics on the passivity of various metals are given; in some it tears off the cover layer, dispersing it in the liquid, in others it has the opposite effect. The anodic passivity of Ni in weakly acid Na_2SO_4 solution is hastened. Explanations are not yet possible.

1068. SCHUBERT, K., AND PFISTERER, H. [Crystal Chemistry of Intermediate Phases Richest in Metals of B Subgroups of Alloys Between Transition Metals of Iron and Platinum Triads and Elements of the Fourth Group.] Ztschr. Metallkunde, vol. 41, 1951, pp. 433-441; Metal Abs., vol. 19, 1952, p. 381; British Abs., 1952, p. B-I-866.

An x-ray study of the phases reveals the structure of the silicides of Ni and Co, showing a CaF_2 type structure at low temperature with $a = 5.39_{\pm 3} \text{A}$ and $5.35_{\pm 1} \text{A}$, respectively. CoSi_2 does not exist. NiSi does not crystallize in a B20 (FeSi)-type structure. Structures of other metal phases are given.

1069. SPACU, P. G. [Complex Vanadates.] Bull. sec. sci. acad. roumaine, vol. 22, 1939, pp. 42-48; Chem. Abs., vol. 34, 1940, p. 5774⁸.

The following complex compound is precipitated on addition of NH_4VO_3 to aqueous MCl_2 , MSO_4 , or $\text{M}(\text{NO}_3)_2$ (where $\text{M} = \text{Cu}$, Co , or Ni) containing $\text{C}_5\text{H}_5\text{N} \cdot [\text{M}(\text{C}_5\text{H}_5\text{N})_4](\text{VO}_3)_2$.

1070. VALENTINER, S., AND BECKER, G. [The Lattice Structure of Nickel.] Naturwissenschaften, vol. 17, 1929, pp. 639-640; Chem. Abs., vol. 23, 1929, p. 5369⁹.

Pure Ni had a cubical face-centered lattice constant of 3.51A U., regardless of heat treatment (up to $1,000^\circ \text{C}$).

HYDRO PURIFICATION AND SEPARATION CEMENTATION AND DISPLACEMENT REACTIONS

1071. BULAKH, A. A., AND DRACHEVSKAYA, R. K. [Photomicrograph of Cementation of Copper by Nickel Powder.] Zhur. Priklad. Khim., vol. 26, 1953, pp. 1225-1226; Chem. Abs., vol. 48, 1954, p. 8089g.

Cementation of Cu by Ni powder was observed under microscope inspection to proceed easily with continuing

growth of Cu trees and without need of cleaning the surface, since each granule of Ni formed a short-circuited galvanic couple of low e. m. f. because of surface heterogeneity or of impurities. The deposition of crystal Cu on the cathodic part of such a couple caused an increase in e. m. f. which, in turn, accelerated further cementation. Cu crystals grew, while current density and polarization decreased.

1072. CHIZHIKOV, D. M., AND KREINGAUZ, B. P. [Cementation (Deposition) of Cobalt From Aqueous Solutions by Metallic Zinc] (in Russian). Izvestiya Akademii Nauk, S. S. S. R., (Bull. Acad. Sciences, U. S. S. R., Sec. Tech. Sci.), March 1950, pp. 394-400; Metals Rev., vol. 23, No. 8, August 1950.

Separation of Co from Ni by deposition on Zn is possible only when the Co concentration in the solution is at least twice that of Ni, at an initial concentration of 1 gm. of Co per liter. Temperature changes and different Co concentrations influence the kinetics of the process of electrodeposition of Co. The method of investigation is described.

1073. DROZDOV, B. V. [Kinetics of the Cementation Reaction.] Zhur. Priklad. Khim., U. S. S. R.; Jour. Applied Chem., vol. 22, 1949, pp. 483-490; Chem. Abs., vol. 43, 1949, p. 7796l.

A theoretical treatment of the rate of the displacement reaction $\text{Cu}^{++} + \text{Ni} \rightarrow \text{Cu} + \text{Ni}^{++}$ is presented, and equations are derived for three phases in the progress of the reaction (1) when the Cu film is loose and offers no resistance to diffusion; (2) in an intermediate stage when the reaction rate is commensurate with the rate of diffusion; (3) in the last stage when reaction rate is determined wholly by diffusion. The slowing down constant B, in the first stage is 0, in the second greater than 0 but less than 1, and in the final stage is 1. At 25° C. the first phase continued for 5 minutes, the second mechanism prevailed for 15 minutes, and the final one for 70 minutes; then the Cu began to dissolve. Large amounts of sodium chloride inhibit the reaction.

1074. FALCONBRIDGE NIKKELVERK AKTIESELSKAP. [Precipitating Iron From Nickel Salt Solutions.] German Patent 573,067, May 17, 1931; Chem. Abs., vol. 27, 1933, p. 2923.

Air is blown into the solution after the latter has been neutralized, neutralization being effected by additive Ni, which has been prepared by treating a compound of Ni with a reducing gas at 350° - 450°C . Cu may be removed from the solution by cementation. The cementation and aeration may be effected at a temperature below 60°C .

1075. FRENTS, G. S., AND KREINGAUZ, B. P. [Kinetics of Deposition of Cobalt and Nickel From Aqueous Solutions by Metallic Zinc.] A. A. Baikov Inst. Metallurgy Acad. Sci., U. S. S. R., Izvest. Akad. Nauk, S. S. S. R. Otdel. Tekh. Nauk., 1947, pp. 1705-1712; Chem. Abs., vol. 42, 1948, p. 8054g.

The rate of deposition of Co and Ni from sulfate solution by Zn was determined at 76°C . The initial concentration of Co ranged from 0.267 to 3.015 gm. and of Ni from 1.038 to 20.5 gm. per l. During the deposition of Co, the pH increased from an initial 3.0-3.5 to pH 6.8 in 3 hr., and the reaction stopped. The amount of metal deposited per unit area of Zn was increased by raising the concentration of Co and Ni and by maintaining the pH at 3.5-4.0. At the same concentration, about twice as much Co as Ni was deposited.

1076. GRONNINGSÆTER, A. M. (assigned to Falconbridge Nickel Mines, Ltd.). Removing Iron From Nickel-Copper Solutions. U. S. Patent 1,986,967, Jan. 8, 1935 (see Norwegian Patent 51,736, Nov. 7, 1932; Chem. Abs., vol. 27, 1933, p. 1462); Chem. Abs., vol. 29, 1935, p. 1377⁴.

An acidic solution containing an objectionable amount of Fe is subjected to the neutralizing and Cu-cementing action of metallic Ni, obtained by gas reduction at a temperature only slightly above that required for reduction.

After enough metallic Ni for neutralization has been added, the solution is aerated, precipitating the Fe.

1077. INTERNATIONAL NICKEL CO., INC. [Nickel.] French Patent 716,845, May 9, 1931 (*see* Chem. Abs., vol. 25, 1931, p. 2678); Chem. Abs., vol. 26, 1932, p. 2163.

A solution containing Ni, Fe, and Cu is treated with a metallic powder having a basis of Ni, so as to provoke not only precipitation of the dissolved Cu but also a reduction in the concentration of H-ions of the solution to a value that permits precipitation of the Fe in the state of hydroxide by subsequent treatment of the solution by air. The added metal containing Ni is obtained by reduction with a gas at a low temperature.

1078. IZGARUISHEV, N., AND MIRKIN, I. [Investigation of the Process of Mutual Replacement of Metals.] *Korrosion u. Metallschutz.*, vol. 10, 1934, pp. 109-112; Chem. Abs., vol. 28, 1934, p. 5317.

The replacement of Cu, Cd, Pb, Ni, Fe, and Co from their salt solutions by Zn in the presence of various anions was investigated. Of considerable effect is development of H₂ in neutral solutions, especially in the presence of Ni, Fe, Co, Cr, and Cl ions. The phenomena are explained by the different overvoltages of H₂ in contact with galvanic cells formed by the precipitation of the various metals on the Zn. A specific activating effect of the various ions upon the hydrogen development is assumed.

1079. KAMECKI, JULIAN, AND SEDZIMER, JERZY. [Precipitation of Metals by Metals in Hydrometallurgy.] *Hutnik*, vol. 19, 1952, pp. 383-388; Chem. Abs., vol. 47, 1953, p. 10,431d.

History, theory, and selection of best conditions for precipitation of metals by metals are described. Examples: Precipitation of Au and Ag from cyanide solution by Zn and Al, precipitation of Cu by Fe from solutions of chlorides or sulfates, and precipitation of Cu, Cd, Ni, and Co by Zn from solution of sulfates. Research is in progress on precipitation of very pure Cu by Fe and obtaining electric energy in an apparatus analogous to the Daniells cell (26 refs.).

1080. LAUSBERG, FRITZ (assigned to Kurt, Albert, G. m. b. H. Chemische Fabriken Werk Neuss). [Disintegrating Alloys.] German Patent 642,563, Mar. 8, 1937 (*Cl. 40b 3.40*); Chem. Abs., vol. 31, 1937, p. 5747.

Alloys which contain more Ni than Cu are subjected to an acid heat treatment under pressure. The temperature of the alloys is first raised to 700°-800° C. then lowered to 140°-160° C. The acid attacks Cu, which is then cemented out by Ni; thus a Cu powder and nickel sulfate are produced.

1081. PIONTELLI, ROBERTO [Electrochemistry of Metals.] *Jour. chim. phys.*, vol. 45, 1948, pp. 115-122 (*see* Chem. Abs., vol. 43, 1949, p. 4959g); Chem. Abs., vol. 43, 1949, p. 7351f, g, h.

Metals are divided into three classes: (1) "Normal" metals, such as Pb, Hg, Tl, Cd, and Sn; (2) "inert" metals, such as Fe, Co, Ni, Cr, Mn, Pt, Rh, and Pd; and (3) those intermediate between (1) and (2), such as Cu, Ag, Au, As, Sb, and Bi. The properties considered are masked by high electropositivity in the alkali and alkaline earth metals.

1082. ———. [Electrochemical Behavior of Metals, a Discussion.] *Ricerca sci.*, vol. 18, 1948, pp. S24-S30; Chem. Abs., vol. 43, 1949, p. 4959g.

1083. ——— (University of Milan, Italy). [Electrical

Properties of Metals and the Metallic Bond.] *Jour. chim. phys.*, vol. 46, 1949, pp. 288-297; *Colloques intern. centr. Nat. recherche sci.* (Paris), No. 18, *Laison chim.*, 1948, pp. 102-111 (pub. 1950) (*see* Chem. Abs., vol. 43, 1949, p. 7351e); Chem. Abs., vol. 44, 1950, p. 8799b.

Metals of normal electrochemical behavior are contrasted with those which are inert. The latter have incomplete electronic sublayers and become more inert as the interatomic distances decrease, the structure of the metallic phase is less open, and the ions are more polarizable. Barrier effects for inert metals depend mainly on the energy of the interionic bonds. The electrochemical behavior of some intermediate metals (Ni, Co, and Fe among others) is discussed in the light of their physicochemical properties.

1084. PIONTELLI, ROBERTO, AND FRACCHIA, PIERLUIGI. [Reactions Involving the Displacement of Tin by Means of Nickel and the Inhibitory Action of Tin.] *Gazz. chim. ital.*, vol. 79, 1949, pp. 280-285; Chem. Abs., vol. 43, 1949, p. 8245g.

Earlier work on the displacement of Sn by Fe (*see* Piontelli and Simonetta, Chem. Abs., vol. 41, 1947, p. 7209d) was extended to a study of the displacement of Sn in stannous chloride in HCl solutions and also containing various concentrations of Ni at different temperatures. Ni in various forms was used including sheet, solid, and powdered electrolytic metal, powder deposited from a nickel chloride bath, and activated, powdered electrolytic Ni. In general, HCl above 5 moles per liter afforded no protection, but under that figure a protective coating of Sn slowed the reaction. Solid electrolytic Ni was the most active of the forms tested.

1085. ———. [Displacement Reactions of Arsenic by Nickel and the Inhibitory Action of Arsenic.] *Gazz. chim. ital.*, vol. 79, 1949, pp. 533-538; Chem. Abs., vol. 43, 1949, p. 8903a.

Work on the displacement of Sn by Ni (Chem. Abs., vol. 43, 1949, p. 8245g) was continued in a corresponding study of As and Ni. In HCl of all degrees of acidity, As in all concentrations was displaced by all types of Ni tested and was deposited in the form of powder, scale, or compact film on the Ni in accord with As and acid concentration. The types of Ni vary in being more or less passive. Temperature has a considerable influence on the displacement reaction but only in the formation of a protective film of As. An electrolytic deposit of As on Ni does not protect the Ni to the same extent from attack by HCl as other forms of deposits listed in the present discussion, probably because of the evening out or leveling action to produce a Ni surface freer from irregularities.

1086. ——— (Politecnico, Milano, Italy). [Displacement Reactions of Arsenic by Iron, Cobalt, and Nickel, and the Inhibitory Effect of Arsenic.] *Gazz. chim. ital.*, vol. 79, 1949, pp. 722-731 (*see* Piontelli and Simonetta, Chem. Abs., vol. 43, 1949, pp. 8903a, 8913d); Chem. Abs., vol. 44, 1950, p. 3816f.

The comparative effects of Fe, Ni, and Co in solutions containing different concentrations of As and HCl (1-11.7 normal) at 50° C. were studied.

Because of its relative nobility and in spite of its cathodic inertia, As is displaced in solution, under all conditions tried, by Fe, Ni, and Co. Fe is less noble than Ni or Co, with a lesser cathodic inertia, and acts accordingly. The reactivity of Co is less than that of Ni. Depositions of As are regular, or irregular, and while a low As concentration has an activating effect, its high concentration is inhibitory.

1087. PIONTELLI, ROBERTO, AND SIMONETTA, MASSIMO. [Studies of the Behavior of Metals in Concentration Cells. V.] *Gazz. chim. ital.*, vol. 79, 1949, pp. 24-30 (*see* Chem. Abs., vol. 43, 1949, p. 8286e); Chem. Abs., vol. 43, 1949, p. 8908b.

The work was extended to Mn, Co, Zn, and Tl with the same apparatus and technique as before. The results, which are given in detail, confirm the electrochemical inertia of Mn and Co and the normal behavior of Zn and Tl in accord with what would be expected in view of their atomic structures.

1088. PLETENEV, Z. A., AND FISHKOVA, T. E. [Separation of Nickel From Its Salt Solutions by Metallic Zinc or Iron.] *Jour. Appl. Chem. (U. S. S. R.)*, vol. 9, 1936, pp. 1394-1399 (in German, p. 1399); *Chem. Abs.*, vol. 31, 1937, p. 1737¹.

Experimental proof is given of the reaction $M + NiSO_4 + 2H_2O = MSO_4 + Ni(OH)_2 + H_2$, where M is Zn or Fe.

Metallic Ni is not deposited because of insufficient H_2 overvoltage on a thin film of Ni surface; H_2 is displaced from solution rather than Ni. If acid is added, containing an equivalent of hydrogen to that evolved, Ni metal is included in the precipitated $Ni(OH)_2$ as shown by a magnet.

1089. RUSSELL, A. S. Order of Affinity of Metals for Copper, Iron, Cobalt, and Nickel. *Nature*, vol. 138, 1936, p. 161; *British Chem. Abs.*, 1936, p. A-1078.

Certain metals show a definite order with respect to their power for combining with Cu, Fe, Co, and Ni. With Co, the most stable compounds are $AlCo$, $SnCo_2$, and $HgCo$, and with Ni, $AlNi$, $SnNi_2$, $ZnNi$, and $HgNi$. The order for Co and Ni is Al, Sn, Zn, Hg, Cd, and Pb. Neither Sn nor Zn can displace Al from $AlCo$ or $AlNi$. However, if Co or Ni is competed for by metals in the series, the earlier one in the series combines, to the exclusion of the others.

1090. SHIMATANI, TAKAO, AND IIO, TOSHIMASA (assigned to Sumitomo Metal Mining Co.). [Purification of Waste Liquor From Nickel Electrolysis.] *Japanese Patent* 5159, Oct. 9, 1953; *Chem. Abs.*, vol. 48, 1954, p. 10,463f.

Waste Ni liquor from Ni electrolysis is largely freed of Cu in the procedure. Pieces of electrolytic Ni, $0.3 \times 2.0 \times 0.5$ cm., are tempered by heating for an hour at 500° C. and placed in a glass tube, through which the solution to be purified is passed at the rate of 1 l. per hr. for 45 hr. The waste liquor containing Ni 39.5, H_3BO_3 24.4, and Cu 0.3329 gm. per l. is thus freed of Cu to produce an effluent containing only 0.0015 gm. Cu per l. To regenerate the contents of the tube, it is treated with 400 ml. of 12-percent NH_4OH for 30 min., after which the solution contains 0.65 gm. Ni per l. and 7.87 gm. Cu per l. Upon draining off this solution, the tube is ready for purification of further solution.

1091. SOCIÉTÉ ANONYME TRÉFILIERIES ET LAMINOIRS DU HAVRE. [Separating Metals From Solutions of Their Salts.] *German Patent* 648,543, Aug. 3, 1937 (*Cl. 12a 1*); *Chem. Abs.*, vol. 31, 1937, p. 8492².

Cementation of Ni metal from its sulfate solution is caused by the addition of granular Al, with an acid to remove the oxide film from the aluminum. H_2SO_4 is used. Fe metal can be similarly precipitated.

1092. UNION CHIMIQUE BELGE (assigned to Société anonyme). [Recovery of Metals.] *French Patent* 760,242, Feb. 19, 1934; *Chem. Abs.*, vol. 28, 1934, p. 3370³.

The cements obtained from the purification of electrolytic zinc solutions are treated to separate Ni and Co and recover Zn, Cu, Cd, and Pb by submitting them to an oxidizing heating at 300°-400° C. and afterwards lixiviating with a solution of $ZnSO_4$.

ION EXCHANGE AND CHROMATOGRAPHY

1093. AUSTERWEIL, G. [The Preparation and Purification of Salts by the Use of Zeolites.] *Compt. rend.*,

vol. 193, 1931, pp. 1013-1016; *Chem. Abs.*, vol. 26, 1932, p. 1716.

Certain salts can be purified by absorption on zeolites, with subsequent displacement. Formulas are developed for the amounts of materials and the number of treatments necessary. The method is applied to the purification of commercial $Co(NO_3)_2$.

1094. BENCH, H. L., WEISBLATT, H. B., AND WINGET, R. H. (Carbide & Carbon Chemical Corp. K-25). Ion-Exchange Equilibria Exchange of Cobaltamine Complex Ions. U. S. AEC Tech. Inf. Branch, Oak Ridge, Tenn., AEC-D-2670, 10/12/49; U. S. Government Publications Monthly Catalog, 1950, item 398.

Throughout the mass of work that has accumulated in the literature on ion-exchange resins, the relative effects of ionic charge and ionic radius on exchange adsorption has been stated in general terms only. The present experimental work is done to clarify this. It has been found that ionic radius rather than ionic charge is the dominant factor.

1095. CARASSITI, VITTORIO (University of Bologna, Italy). [Electrophoresis of Inorganic Complexes in Solution. I. Ionic Mobility Measurements on Some Complexes of Trivalent Cobalt by the Moving Boundary Method.] *Gazz. chim. ital.*, vol. 84, 1954, pp. 405-419; *Chem. Abs.*, vol. 48, 1954, p. 13,515f.

The complexes $[Co(NH_3)_4(NO_2)_2]Cl(I)$, $[Coen_2Cl]Cl(II)$, $[Coen_2(NCS)Cl]Cl(III)$, and $[Coen_2(NO_2)_2]NO_3(IV)$ were investigated in a Tiselius electrophoresis cell (described in detail), in 0.02 M aqueous solutions at 1.00° C.; the indicator ions were pyramidone HCl (0.015M) and triethanolammonium formate (0.012M). The ionic mobilities were measured in 10^{-4} cm.² sec.⁻¹ volt.⁻¹. In the same order as above, the results were cis-I, 0.93; trans-I, 1.37; cis-II, 1.18; trans-II, 1.26; cis-III, 1.04; trans-III, 1.40; cis-IV, 1.02; and trans-IV, 1.41. The greater mobility of the trans isomers is ascribed to a smaller hydration number.

1096. FLAGG, J. F. The Nonexchange of Cobalt in Certain Complex Salts. *Jour. Am. Chem. Soc.*, vol. 63, 1941, pp. 557-559; *Chem. Abs.*, vol. 35, 1941, p. 2086².

No exchange between radioactive cobaltous ion and $[Co(NH_3)_4]NO_3$, $[Co(NH_3)_4]Cl$, $[Co(NH_3)_4]Cl_2$, $[Coen_2Cl]Cl$ (pn=propylenediamine), $[Co(NH_3)_4(NO_2)_2]$, and $[Co(NH_3)_4(NO_2)_2]Cl$ was found within the limits of experimental error. It is probable that the reduction of cobaltic ion by water is more rapid than the exchange reaction. No exchange of Co atoms in cobaltous cobalticyanide was found.

1097. FRICKE, R., AND SCHMÄH, H. [Separation of Cobalt From Iron and Copper by Chromatography. The Water Solubility and Alkali Zeolitic Properties of Aluminum Hydroxide.] *Ztschr. anorg. Chem.*, vol. 255, 1948, pp. 253-268; *Chem. Abs.*, vol. 43, 1949, p. 2070h.

The solubility at 18° C. of very pure $Al(OH)_3$ in H_2O is too low to be measured by spectrophotometry with eriochrome cyanine, and by conductivity measurement is less than 10^{-6} mol. per l., a value lower than previous measurements indicated.

The surface of very pure aluminum hydroxide has basic properties and shows hydrolytic absorption of potassium chloride, sulfate, and perchlorate up to pH 9. It may also be used for chromatographic separation of ferric sulfate, copper sulfate, and cobaltous sulfate. The Fe salts are in the upper zone, Cu in the middle, and Co below, as might be expected from their base strengths.

1098. FRONAEUS, STURE (University of Lund, Sweden). The Application of the Mass-Action Law to Cation Exchange Equilibria. *Acta chem. scand.*, vol. 7,

1953, pp. 469-480 (in English); Chem. Abs., vol. 48, 1954, p. 7999e.

The mass-action law, applied to cation exchange equilibria, sometimes gives mass-law products which are dependent on the ionic composition of the exchanger, even when variations in the rational activity coefficient are not appreciable. A theory for the variation is given, based on the assumption that small amounts of a fixed group with great affinity for certain cations are present in the exchanger. Measurements on the exchanges $\text{Cu}^{++}-\text{Na}^{+}$ and $\text{Ni}^{++}-\text{Na}^{+}$ on Amberlite 1R-105 are in agreement with the theory and show that the groups have a great proton affinity. The presence of these groups was shown independently by pH titrations, and it is presumed that they are carboxylate groups.

1099. GAPON, T. B., AND GAPON, E. N. [Precipitation Chromatography.] A. I. Mikoyan Tech. Inst. Fis. Ind., Moscow. Doklady Akad. Nauk., S. S. S. R., vol. 60, 1948, pp. 401-404; Chem. Abs., vol. 42, 1948, p. 6603i.

In contradistinction to absorption chromatography, the method of precipitation chromatography uses columns made up of a carrier (Al_2O_3 , $\text{Al}(\text{OH})_3$, SiO_2 gel, etc.) mixed with a precipitating agent. The column can be used either dry or wet. (1) A dry column of SiO_2 gel with sodium silicate as precipitant, prepared by mixing (mechanically) Na_2SiO_3 , 1 part: SiO_2 , 9 parts was prepared. After 12 hr. of filtration of mixed solutions of nitrates, mostly 0.5 N, and washing without pressure, 2 colored zones were visible—upper Cu^{++} plus Co^{++} blue (sharp boundary) pink; Cu^{++} plus Ni^{++} blue (sharp boundary) green and others. (2) A dry column of Al_2O_3 with KI as precipitant is described, with its uses. (3) Dry column Al_2O_3 with Ag_2SO_4 . Three other columns and their uses are detailed. Operations can be reversed, first solution, then precipitant, being poured in.

1100. GLÜCKAUF, E., AND COATES, J. I. (University of Durham, England). Theory of Chromatography. IV. The Influence on Incomplete Equilibrium on the Front Boundary of Chromatograms and on the Effectiveness of Separation. Jour. Chem. Soc., 1947, pp. 1302-1308 and 1315-1321 (see Chem. Abs., vol. 40, 1946, p. 6932²); Chem. Abs., vol. 42, 1948, p. 2490e.

The effects of self-sharpening and of nonequilibrium on the final form of the front boundary are discussed, and equations are derived. Curves are shown for developing Mn and Cu bands from mixtures on alumina by H_2SO_4 , and of Cu and Co on alumina by manganous sulfate.

1101. HALL, N. F., AND WILLEFORD, B. R., JR. Exchange Reactions of Some 4-Coordinated Nickel Complexes. Jour. Am. Chem. Soc., vol. 73, 1951, pp. 5419-5423; British Abs., 1952, p. A-1-191.

The exchange reactions of 14 4-coordinated Ni complexes are studied with radioactive NiCl_2 in solution at room temperature. Results are correlated with published magnetic susceptibilities and other measurements indicative of the types of bonds present. Four compounds, which are paramagnetic in the solid state, exchange readily; 5 diamagnetic complexes exchanged, and 5 others did not. Ethylenediamine confers special inertness on certain complexes containing it. A previous correlation (Johnson and Hall, work cited above, vol. 70, 1948, p. 2344) between rate of Ni exchange and rate of Ni precipitation with dimethylglyoxime is confirmed and extended. A comparison is made of the rate of exchange of the central atom in certain complexes of Cu and Ni.

1102. HERBER, R. H., AND IRVINE, J. W., JR. (Massachusetts Institute of Technology, Cambridge). Anion-Exchange Studies. I. Bromide Complexes of

Co(II), Cu(II), Zn(II), and Ga(III). Jour. Am. Chem. Soc., vol. 76, 1954, pp. 987-991; Chem. Abs., vol. 48, 1954, p. 7476f.

By anion-exchange in HBr solutions, with Dowex-1, separation of the complexes of these elements is feasible. Except for Ga(III), the behavior of the bromide complexes parallels that of the chloride complexes. The distribution coefficient for Ga(III) between the solid and aqueous phases is a function of concentration. The studies did not extend beyond approximately 7M HBr because of the reaction of the resin with the eluant.

1103. JACOBS, P. W. M., AND TOMPKINS, F. C. Ionic Chromatography. I. Static Adsorption Measurements. Trans. Faraday Soc., vol. 41, 1945, pp. 388-394; Chem. Abs., vol. 39, 1945, p. 5157¹.

Five grams of alumina, prewashed with 100 ml. of distilled water and heated for 1 hr. at 480° C. and cooled over a saturated salt/sugar solution, was used immediately as adsorbent. Isotherms for both cations and anions were approximately expressed by the Freundlich expression and by the equation $Q=k_1+k_2 \log C$. Adsorbates were sulfates of Ni and Co among others. The cation was more strongly adsorbed than the anion, which may be explained by the amphoteric functioning of alumina.

II. Position, Rate of Advance, and Width of Adsorbate Zones. The volume of 0.1 N solutions of cations which traversed columns of equal length until detected in the filtrate was determined. It was found that $C_0/Q(d\epsilon/dt)_{C_0} = \text{constant}$, where ϵ is any distance from the top of the column at time t , C_0 the initial concentration, and Q the amount of solute adsorbed per unit length of column. In the presence of an acid, the amount adsorbed decreases and the band widens.

III. Elution Curves. The concentration distribution of solute over the band width was studied, using H_2SO_4 at 20 milliequivalents per liter. The initial concentration, volume of solutions, length of column, and pH were investigated. It was concluded that alumina was unsuitable as an adsorbent from the view of separability of cations and of quantitative applications.

1104. KAMDMONTZEFF, IRENE. [The Separation of Transition Elements on a Cationic Ion-Exchanger, and the Phenomenon of "Tailing" During Elution. I. The Case of Nickel-Cobalt.] Jour. chim. phys., 1954, pp. 197-200; Chem. Abs., vol. 49, 1955, p. 33a.

Co and Ni were separated on ion-exchange resins (Dowex 50, Amberlite 1R100, and Ion X) by the use of columns packed with resins of different mesh size. The concentration of the solution used to apply the ions to the exchange resin and the pH of the eluting HCl solution are important factors that determine the sharpness of the separation. "Tailing", the slow elution of adsorbed ions, is explained on the basis of slow diffusion from the interior of exchange resin particles. Good separation of Ni and Co was obtained with a 45×0.7 -cm. column packed with 120- to 150-mesh Amberlite 1R-100. The ions (as chlorides) were fixed on the column at a concentration of 0.05 M (8 mg. NiCl_2 and CoCl_2) and were eluted, with good separation, by 0.3 N HCl flowing at the rate of 9 ml. per hr. About 1,000 ml. of eluent was used.

1105. KING, E. L., AND WALTERS, R. R. (University of Wisconsin, Madison). The Ion-Exchange Separation of Isomeric Dinitrotetrammine Cobalt (III) Ions. Jour. Am. Chem. Soc., vol. 74, 1952, pp. 4471-4472 (see Chem. Abs., vol. 46, 1952, p. 6981a); Chem. Abs., vol. 48, 1954, p. 13,515e.

Cis- and trans-dinitrotetrammine cobalt (III) ions were prepared, and their elution characteristics were determined by means of their absorption spectra. The trans- is more easily eluted than the cis-form. The trans-isomer has no dipole moment; the cis-isomer has

one. Presumably, the more polar ion is held more strongly in the resin phase.

1106. KOSAKA, YUJIRO, AND SATO, AKIRA (Tokyo Metropolitan University). [Continuous Ion Exchange. II. Removal of Nickelous and Ferric Ions From Aqueous Solution by Electrolytic Continuous Ion Exchange.] *Jour. Chem. Soc., Japan, Ind. Chem. Sec.*, vol. 56, 1953, pp. 159-160 (*see Chem. Abs.*, vol. 48, 1954, p. 6623b); *Chem. Abs.*, vol. 48, 1954, p. 9239f.

A continuous electrolysis was tried with columns of ion exchangers (Amberlite 1R-120 and 1RA-400) from both sides of which the electrical potentials of 100 to 200 volts were applied. At a current of 0.2 to 3.0 ma. per cm.² and a space velocity of 5 to 50 cc. per cc. hour of the aqueous solutions containing 10^{-2} to 10^{-4} N Ni^{++} or Fe^{+++} the efficiency of removal was 50 to 100 percent. The diluted solution was easily purified; the solution weaker than 10^{-3} N could be treated at 100-200 v. and 10 cc. per cc. hour. The presence of a precipitating chamber beside the exchanger columns was recommended. The removal of Fe^{+++} was slightly more difficult than that of Ni^{++} .

1107. KOZAK, R., AND WALTON, H. F. (Northwestern University, Evanston, Ill.). Separation of Metal Ions by Cation Exchange. *Jour. Phys. Chem.*, vol. 49, 1945, pp. 471-472; *Chem. Abs.*, vol. 40, 1946, p. 2371¹.

Using "Zee-Karb", a sulfonated coal, as the exchange medium, an attempt to separate Ni from Cu, Cd from Zn, and Ag from Co by cation exchange was improved by lengthening the column from 2 to 6 feet but was considered impractical, because it did not give quantitative separation.

1108. KUWADA, TSOTOMU, AND YOSHIKAWA, SADAQ. [Separation of Iron and Nickel by Use of Anion-Exchange Resin.] Japanese Patent 1564, Apr. 15, 1953; *Chem. Abs.*, vol. 48, 1954, p. 2996g.

A solution of 75 gm. of melamine, 400 gm. of 36-percent formalin, and 300 gm. of water at 90°-95° C. is treated with 50 ml. 1 N NaOH, stirred 4 to 6 hr., and the granular product is washed with water and dried to give 110 gm. of resin, 50 gm. of which is treated with a mixture of 150 gm. of 36-percent formalin, 25 gm. of 10-percent HCl, and 100 gm. of MeNH_2 for 3 hr. at 90°-95° C. The solution is drained, and the product is washed with water to give anion-exchange resin. One liter of solution recovered from Ni catalyst and containing 0.25 gm. of Fe^{+++} , 7.25 gm. of Ni^{++} , and SO_4^{--} is passed through 27 ml. of the resin activated with 1 N NH_4OH to absorb Fe^{+++} in the resin and to give Ni^{++} in the effluent. The resin is regenerated by treating with normal H_2SO_4 and NH_4OH .

1109. MOORE, G. E., AND KRAUS, K. A. (Oak Ridge National Laboratory, Oak Ridge, Tenn.). Anion-Exchange. IV. Cobalt and Nickel in Hydrochloric Acid Solutions. *Jour. Am. Chem. Soc.*, vol. 74, 1952, pp. 843-844; *Chem. Abs.*, vol. 47, 1953, p. 4166f.

The anion-exchange behavior of Ni(II) and Co(II) in 0.5 to 12 molar HCl was studied by determining their elution constants, $E=dA/V$, where d is the distance (centimeters) the adsorption band moves when V milliliters of eluent has passed through a column of A cm. Dowex-1 was used. The difference in the adsorption behaviors of Ni and Co is sufficient to permit excellent separation.

1110. NAPOL'SKII, S. A. [Electrophoretic Chromatography.] *Issledovaniya v Oblasti Khromatog.*, Trudy Vsesoyuz. Soveshchaniya Khromatog., Akad. Nauk., S. S. R., Otdel. Khim. Nauk., 1950, pp. 147-154 (pub. in 1952); *Chem. Abs.*, vol. 48, 1954, p. 2495e.

Detailed descriptions of experiments with chromatography of electrolytes in a tube passing direct current was given. Usually, 0.1 N NaCl or Na_2SO_4 electrolyte

was employed. Since the pH level varied from one electrode to the other, numerous common reactions were modified. Thus, with Co salts, no deposition of Co on the cathode took place, while a blue zone formed which grew toward the anode; with increased current density the blue zone moved to the anode, becoming red on the frontal side and nearly brown at the anode. Similar phenomena were seen with Ni and Cu sulfates. Often the adsorbing properties of an adsorbent altered after preliminary passage of direct current. Cations moving from the anode did not reach the cathode, but stopped a certain distance from it, forming a well-defined boundary. The order of various cations is the same as with a filtration chromatogram, but lower cation concentration was allowable and sharper bands formed.

1111. NODDACK, W., AND BANKMANN, E. (Geochemical Institut, Bamberg, Germany). [Chromatography of the Heavy Metal Ions on Aluminum Oxide.] *Ztschr. Elektrochem.*, vol. 58, 1954, pp. 725-731; *Chem. Abs.*, vol. 49, 1955, p. 5069b.

The following order of cations from top to bottom of the gamma- Al_2O_3 column, was observed: Th^{++} , Ce^{++} , Fe^{+++} , Ga^{+++} , and In^{+++} , Al^{+++} , Cr^{+++} , Hg^{++} , UO_2^{++} , Cu^{++} , Pb^{++} , Zn^{++} , Ni^{++} , Co^{++} , Fe^{++} , and Cd^{++} , Mn^{++} , and Ag^+ , Ti^+ . The mechanism of ion separation on Al_2O_3 columns is considered. The roles of ionic radius, ion potentials, hydrolysis, hydration, and diffusion coefficient are considered (55 refs.).

1112. OKA, YOSHINAGA, AND MURATA, AKIRA. [Quantitative Inorganic Chromatography. IV. Chromatographic Separation of Some Acids and Salts on Alumina-Impregnated Paper.] *Tôhoku Univ. Ser. A.*, vol. 5, 1953, pp. 343-349, Anal. (*see Chem. Abs.*, vol. 47, 1953, p. 2631f); *Chem. Abs.*, vol. 48, 1954, p. 7480f.

The chromatographic separation of H_2SO_4 , HNO_3 , and Cu, Zn, Cd, Pb, Mn, Ni, and Co sulfates and nitrates by the use of paper impregnated with Al_2O_3 and H_2O development was studied.

1113. SACCONI, LUIGI. [III. Influence of Ionic Hydration on Chromatographic Adsorption Chromatography of Complex Cobaltamminic Compounds. Inorganic Chromatographic Adsorption.] *Gazz. chim. Ital.*, vol. 79, 1949, pp. 152-164 (*see Chem. Abs.*, vol. 43, 1949, p. 2542a); *Chem. Abs.*, vol. 43, 1949, p. 8295b.

Adsorption of cobaltammino complexes on activated alumina is governed chiefly by the dimensions and polarizability of the coordinated radicals; the ionic hydration is a fundamental factor. Adsorption of ions on alumina depends on the coordinated groups around the cations formed either from simple salts (aqueous ions) or from complex salts. Forms of alumina having the highest absorptive capacity have the greatest tendency to become hydrated. Highly active alumina evolved 20 times as much heat as pure alumina. A Co complex chromatographic series is given, with a list of Co complexes prepared.

1114. SCHIKORE, WERNER, AND MÜLLER, E. G. [Adsorptive Purification in Phosphorescence Chemistry.] *Ztschr. anorg. Chem.*, vol. 255, 1948, pp. 327-330; *Chem. Abs.*, vol. 43, 1949, p. 1659e.

The chromatographic adsorption method used by Tiede and Schikore (*Chem. Abs.*, vol. 37, 1942, p. 3347²) to remove Fe and Cu from zinc sulfate used in making zinc sulfide is adapted to the removal of Ni and Co. Ammoniacal zinc sulfate is passed through a column containing alumina pretreated with an alcoholic solution of dimethylglyoxime (for Ni) or alpha-nitroso-beta-naphthol (for Co) or alumina sandwiched about with a layer of the solid reagent.

1115. SHEMYAKIN, F. M., MITSSELOVSKII, E. S., AND ROMANOV, D. V. [Physicochemical Analysis of the

Kinetics of Chromatographic Adsorption of Cations on Aluminum Oxide, Zeolite, and Organic Adsorbents.] *Izvest. Sektora Fiz. Khim. Anal. Akad. Nauk., S. S. R.*, vol. 23, 1953, pp. 334-340; *Chem. Abs.*, vol. 48, 1954, p. 9151a.

Chromatographs were obtained for pairs of salts taken from among CuSO_4 , CoSO_4 , $\text{Cr}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$, and $\text{Fe}(\text{NO}_3)_3$. In each series the concentration of one of the pairs of salts gradually increased, while the concentration of the other salt gradually decreased. For each concentration, a curve was plotted giving the change in width of the chromatographic band with time, and for each pair a curve was plotted giving the effect of the concentration on the width of the band. As adsorbents were used Al_2O_3 , zeolite, 8-hydroxyquinoline, betanaphthoquinoline, and cupferron. The experimental results were used for testing the applicability of the Tsvet formula to the rate of change of the width of the band. The formula is $x_t = x(l - e^{-Kt})$, where x_t is the width of the band at the time t and x is the limiting width. K calculated on Al_2O_3 , $K_{\text{Fe}^{+++}} = 0.21$, $K_{\text{Cu}^{+++}} = 0.18$, and $K_{\text{Co}} = 0.15$; on zeolite $K_{\text{Cu}} = 0.55$, and $K_{\text{Co}} = 0.43$. The results for organic adsorbents were similar.

1116. SHIBATA, MURAJI. [The Chromatographic Adsorption of Metallic Ions.] *Tokyo Inst. Technol. Science (Japan)*, vol. 19, 1949, pp. 570-571; *Chem. Abs.*, vol. 45, 1951, p. 7845f.

When an aqueous solution of metallic ions is allowed to pass through a layer of Al_2O_3 , chromatographic adsorption occurs in the following order: Bi^{3+} , Fe^{3+} , Hg^{2+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Cd^{2+} , Ni^{2+} , Fe^{2+} , and Mn^{2+} . A new aspect was obtained from the assumption that the ions were adsorbed by electrostatic forces on the uniformly charged surface of the Al_2O_3 . If the ionic charge is Ze , the charge of Al_2O_3 is $-e$ and the distance R , the potential energy, $-Ze^2/\epsilon R$ should hold a definite relation to the adsorbability of the ion. If the values $-Ze^2/\epsilon R$ are calculated, with the radius of the hydrated ion as R , their order of magnitude agrees well with the order of chromatographic adsorption.

1117. SPECKER, HERMANN, AND HARTKAMP, HEINZ (Institut der Spektrochemie, Dortmund, Germany). [Separation of Iron From Other Cations by Ion Exchange on Alginic Acid.] *Naturwissenschaften*, vol. 40, 1953, pp. 410-411; *Chem. Abs.*, vol. 48, 1954, p. 6905i.

Alginic acid (poly mannuronic acid) will retain Fe^{+++} from mixtures with other ions like Cu^{++} , Mg^{++} , Ni^{++} , Al^{+++} , and UO_2^{++} almost quantitatively; the eluate (HCl , H_2SO_4 , and AcOH) contains only traces of Fe . A column height of 30 cm. was used, diameter 0.8 cm., 3 to 3.5 gm. of dry acid of screen size Din 20. Fe is also quantitatively removed from sulfate solutions before gravimetric assay.

1118. WEST, B. O. (University of Adelaide). Bond Type in Certain Cobalt Complex Compounds. IV. Exchange Reactions of Quadridentate Complexes. *Jour. Chem. Soc.*, 1954, pp. 395-400 (*see Chem. Abs.*, vol. 47, 1953, p. 6271a); *Chem. Abs.*, vol. 49, 1955, p. 7434i.

Exchange of cobaltous ion is reported with N,N' -disalicylideneethylenediaminecobalt(II) and with N,N' -disalicylidene-o-phenylenediaminecobalt(II) in pyridine solution. Experiments were done in nitrogen to avoid absorption of oxygen. With the first compound, exchange is of the first order with $t_{1/2} = 19.5$ minutes at 15°C . With the second compound, exchange is second order. Runs were made over a 10-fold concentration range. Rates are higher than expected from supposed electronic structure as inferred from magnetic susceptibility. The exchange mechanism is discussed.

1119. ——— (University of Adelaide, Australia). Exchange in Cobalt Chelate Compounds. *Nature*, vol.

165, 1950, pp. 122-123; *Chem. Abs.*, vol. 44, 1950, p. 4299f.

Exchange by an ion mechanism between Co and Co chelate compounds exhibiting high paramagnetism was shown by mixing equimolar (with respect to Co) solutions of chelate and cobaltous sulfate, which contained Co isotope 60, separating, and then measuring the activity of the chelate extract. Salicylaldehyde and guaiacol derivatives showed exchange. The unexpected activity of the chelate layer obtained with the salicylaldehyde complex was attributed to the possibility of the formation of an exchangeable compound. No exchange was found in the ethylenediamine complex, which was strongly diamagnetic.

1120. ——— (University of Adelaide, Australia). Bond Type in Certain Cobalt Complex Compounds. V. The Exchange Reactions of Cobaltous 1,10, Phenanthroline and Tripyridyl Complexes. *Jour. Chem. Soc.*, 1954, pp. 578-579; *Chem. Abs.*, vol. 49, 1955, p. 7435a.

The exchange of cobalt ions with [tris(1,10, phenanthroline) cobalt (II)] $^{2+}$, [tris(5-methyl, 1,10, phenanthroline) cobalt (II)] $^{2+}$ and [tris(5-nitro 1,10, phenanthroline) cobalt (II)] $^{2+}$ is very rapid at 15°C . and 0.005 M. With [bis(tripyridyl) cobalt (II)] $^{2+}$ exchange is slow, $t_{1/2} = 2.8$ hr. It is concluded that the phenanthroline complexes have ionic or weakly covalent bonding, as suggested by magnetic evidence. Greater stability of the bistripyridyl complex may be due to greater number of chelate rings per molecule.

1121. ZOLOTAVIN, V. L. [Chromatographic Series of Cations.] *Sbornik Statei Obschei Khim. Akad. Nauk., S. S. R.*, vol. 1, 1953, pp. 34-36 (*see Schwab and Jockeks, Chem. Abs.*, vol. 31, 1937, p. 6993 ^{4}); *Chem. Abs.*, vol. 48, 1954, p. 12,508b.

A procedure for establishing the chromatographic order of cations is described in which zones on filter paper saturated with $\text{Al}(\text{OH})_3$, and to which drops of solution containing the cations are applied, are treated with suitable indicators to show the presence of the cations. The following order was established: Hg^+ , Hg^{++} , Bi^{+++} , Fe^{++} , (Pb^{++} and UO_2^{++}), Cu^{++} , Ag^{++} , (Cd^{++} and Zn^{++}), Ti^+ , Fe^{++} , (Ni^{++} and Co^{++}), Mn^{++} , Cr^{+++} .

ADSORPTION STUDIES

1122. ERISTAVI, D. I. [Adsorption of Nickel and Cobalt From Aqueous Solutions by Manganese Dioxide and Manganese Ores of Chiatur.] *Kolloid Zhur.*, vol. 10, 1948, pp. 322-328; *Chem. Abs.*, vol. 43, 1949, p. 7774i.

Manganese dioxide adsorbed approximately equal amounts of Co and Ni from solutions of their chlorides or nitrates; at the highest concentration used (1.7 M) approximately 6 milliatoms of Ni or Co were adsorbed by 1 gm. of MnO_2 independently of the method of preparation of manganese dioxide (6 methods were used). The adsorption is cationic (that is, the anion is not adsorbed) and is reversible. Various manganese dioxide and carbonate ores adsorb more Ni than Co. This may explain the greater percentage of nickel oxide (0.04 to 0.09 percent) than of cobaltous oxide (less than 0.003 percent) in ores.

1123. HERMAN, J. [Auto-Oxidation of Iron, Manganese, and Cobalt Hydroxides.] *Compt. rend.*, vol. 202, 1936, pp. 419-420 (*see British Abs.*, 1935, p. A-834); *British Abs.*, 1936fi, p. A-691.

The amount of O_2 absorbed by $\text{Fe}(\text{OH})_2$ precipitated by KOH from excess of FeSO_4 in an atmosphere of O_2 increases with time to attain a limiting value in 2 minutes. This amount is greater than that corresponding to the transformation into Fe^{3+} . With MnSO_4 , there is a rapid initial absorption, followed by a slow reaction proportional to the time, attaining a limit corresponding approximately with the conversion into Mn^{3+} . If excess KOH is present, however, this state is passed.

With excess of CoSO_4 , a green precipitate is obtained that is almost nonoxidizable under the conditions investigated. The same results were obtained with the corresponding chlorides.

1124. KOLTHOFF, I. M., AND OVERHOLSER, L. G. Studies of Aging and Coprecipitation. XXVIII. Adsorption of Bivalent Ions On, and Coprecipitation With. Ortho- $\text{Fe}(\text{OH})_3$, in Ammoniacal Medium. XXIX. The Aging of Ferric Hydroxide in the Absence and Presence of Bivalent Ions in Ammoniacal Medium. Jour. Phys. Chem., vol. 43, 1939, pp. 767-789 and 909-922 (see Chem. Abs., vol. 33, 1939, p. 5722⁵); Chem. Abs., vol. 33, 1933, p. 9084².

The adsorption and coprecipitation of Zn, Ni, or Co decrease with increasing NH_3 and NH_4Cl concentration. The coprecipitation of Zn, Ni, or Co at room temperature is slightly less than at 98° C. and slightly greater than their adsorption when the metals are added immediately after the precipitation of $\text{Fe}(\text{OH})_3$. When ortho- $\text{Fe}(\text{OH})_3$ formed at room temperature was aged in ammoniacal medium in the presence of Zn, Ni, or Co, the amount of metal removed from solution increased slowly on standing at room temperature, but rapidly when aged at 98° C. with low NH_4Cl concentration. The aging of ortho- $\text{Fe}(\text{OH})_3$ was inhibited by the presence of Zn, Ni, Co, or Mg. The inhibiting effect was attributed to a blocking of the hydroxyl group in the polymerization of the $\text{Fe}(\text{OH})_3$.

1125. KURBATOV, M. H., WOOD, G. B., AND KURBATOV, J. D. Isothermal Adsorption of Cobalt From Dilute Solutions. Jour. Phys. Colloid Chem., vol. 55, 1951, pp. 1170-1182 (see British Abs., 1939, pp. A-I-415, A-I-607; and 1946, p. A-I-81); British Abs., 1952, p. A-I-93.

The adsorption of Co on $\text{Fe}(\text{OH})_3$ in the presence of NH_3 and NH_4Cl is studied by the coprecipitation method at low concentrations of Co (10^{-5} to 10^{-6} M) and at gram-atomic ratios of $\text{Fe}:\text{Co}=10^{-5}:10^{-6}$. All analyses were made by means of radioactive Co tracers. The effects of pH, salt concentration, and quantity of adsorbent on the amount of Co adsorbed from solutions of equal Co concentration are studied. Indications are that the adsorption follows the mass law and that there is a region where Henry's law is valid.

$$K = \frac{y(\text{H}_2\text{O})^x}{(1-y)(\text{gm. atom. of Fe})^x}$$

where y = fraction of Co adsorbed, and $x=1.2$ (equivalents of H^+ displaced by 1 gm.-atom of Co on adsorbent). The effects of NH_4^+ , NH_3 , and OH^- may be represented by H_2O in the aqueous solution. The Co adsorbed probably is a mixture of bivalent and partly hydrolyzed bivalent ions having a residual unit charge, or the charge on Co may be partly satisfied by the solid phase and partly by anions in solution.

1126. NAKAHARA, AKITSUGU, AND OTHERS (Osaka University). [Coagulation of Ferric Hydroxide Solution by Metallic Complex Salts.] Jour. Chem. Soc., Japan, Pure Chem. Sec., vol. 74, 1953, pp. 488-490; Chem. Abs., vol. 48, 1954, p. 1191d.

Complex salts having anions containing Co, Fe, Cr, Ni, and Hg coagulate $\text{Fe}(\text{OH})_3$ solution to an extent determined by the electric charge on the complex ion.

1127. SMITH, G. W. The Adsorption of Complex Ammonia Ions on Silica Gel. Jour. Phys. Chem., vol. 43, 1939, pp. 637-646 (see Chem. Abs., vol. 28, 1934, p. 2591⁹); Chem. Abs., vol. 33, 1939, p. 5261².

Adsorption from solutions both of single ions and of mixtures decreased in the order: $\text{Zn}(\text{NH}_3)_4^{++}$, $\text{Cu}(\text{NH}_3)_4^{++}$, $\text{Ni}(\text{NH}_3)_4^{++}$, $\text{Ag}(\text{NH}_3)_2^{+}$. $\text{Ag}(\text{NH}_3)_2^{+}$ was adsorbed most rapidly. In mixtures, the decrease in

the adsorption of each ion is greater in the presence of highly adsorbable ions.

1128. STROMBERG, A. G., DITYATKOVSKAYA, R. V., AND MILOVANOV, N. V. [Polarographic Determination of Copper and Nickel in Steel.] Zavodskaya Lab., vol. 14, 1948, pp. 919-925; Chem. Abs., vol. 43, 1949, p. 2544b.

The adsorption of cupric and nickelous ions by hydrated ferric oxide was studied by a polarographic method with respect to the effect of ammonia, ammonium salts, and amounts of Fe, Cu, and Ni. A precipitate of hydrated ferric oxide adsorbs 2 to 2.5 times more nickelous ions than cupric ions, and the adsorption is increased by lowering the concentration of ammonia or ammonium chloride. But at the 2 points with ammonium chloride at 0.3 N and ammonia at 4.0 N, and also at 0.7 N ammonium chloride and ammonia at 2.5 N, the adsorption of Cu is almost nil. The amount of adsorbed Cu is proportional to the amount of the Fe precipitate, while the adsorption of Ni increases somewhat slower; the amount of adsorption is directly proportional to the concentration of Cu or Ni, respectively. (This is contrary to Thanheiser and Maasen, Chem. Abs., vol. 31, 1937, p. 4615³.)

1129. VAN ITTERBEEK, A., AND VAN DINGENAN, W. [The Formation of Methane in Connection With the Activated Adsorption of Hydrogen and Carbon Monoxide by Nickel and by Copper.] Physica, vol. 8, 1941, pp. 810-824; Chem. Abs., vol. 36, 1942, p. 6062².

1130. VENTURELLO, GIOVANNI (Politecnica, Turin, Italy). [Ion Adsorption by Aluminum Hydroxide.] Atti. reale accad. sci. Torino, Classe sci. fis. mat. nat., vol. 79, 1943-1944, pp. 275-287; Chem. Abs., vol. 41, 1947, p. 4992f.

When a solution of aluminum sulfate containing Cu and Ni ions is precipitated with ammonium hydroxide, the adsorption of the ions by the precipitate follows the law of Freundlich if the solution is dilute enough; in the presence of large amounts of ammonium hydroxide or ammonium salts, the adsorption decreases probably because of the formation of such complex ions as $\text{Cu}(\text{NH}_3)_4^{++}$, which have a greater ionic radius and are less adsorbed. The precipitate and washed aluminum hydroxide have a lower adsorbing power.

MISCELLANEOUS HYDRO OPERATIONS

1131. ASTAKHOV, K. V., AND VERENIKIN, V. B. [Some Inner Complex Compounds of Nickel and Cobalt.] Sbornik. Statel po Obschei Khim. Akad. Nauk. S. S. R., vol. 2, 1953, pp. 1149-1157 (see Chem. Abs., vol. 46, 1952, p. 10,091h); Chem. Abs., vol. 49, 1955, p. 2929f.

Nickel carbonate and sodium ethylene-diaminetetraacetate heated on the water bath give a complex, which is isolated by evaporation at 40°-50° C. as $\text{Na}(\text{NiC}_{10}\text{H}_{12}\text{O}_{16}\text{N}_2) \cdot 2\text{H}_2\text{O}$, and some of its properties are examined. A similar reaction with CoCO_3 gives $\text{Na}_2(\text{CoC}_{10}\text{H}_{12}\text{O}_{16}\text{N}_2) \cdot 2\text{H}_2\text{O}$, which does not lose H_2O even at 80°-90° C., is stable to NaOH, and decomposed by Na_2S and acids. Ni replaces Co in the Co complex when treated with Ni ion. These compounds can be used for separating and determining Ni and Co mixtures. A mixture of the nitrates is treated with portions of sodium-ethylenediaminetetraacetate until all of the Ni has entered the complex. The solution is then treated with NaOH to precipitate $\text{Co}(\text{OH})_2$, which is found to contain no Ni.

1132. BERCOVICI, LEON (assigned to Société Générale Métallurgique de Hoboken). The Separation of Nickel From Solutions Containing Cobalt and Nickel.

British Patent 650,595, Feb. 28, 1951; Chem. Abs., vol. 45, 1951, p. 5601e.

Nickel is removed from Ni- and Co-containing solutions by selective cementation by using iron sulfide, or compounds of Fe with Se, Te, As, or Sb. In an example, 1 l. of a slightly acid solution containing 55 gm. of Co and 350 mg. of Ni is treated with 50 gm. of commercial 200-mesh FeS, under agitation at 90°–100° C. for 3 hr. After the precipitate is filtered, the filtrate contains only 22 mg. of Ni and 54.5 gm. of Co. Hence, the Ni : Co ratio was changed from an original value of 0.65/100 to 0.04/100.

1133. BEVERINI, RAOUL, AND RAYMOND, ELIE. [Separating Nickel and Cobalt.] French Patent 786,810, Sept. 10, 1935, and French Patent 786,868, Sept. 11, 1955; Chem. Abs., vol. 30, 1936, p. 715°.

Nickel and Co solutions are treated with ethanalamines or with glycerolamines in alkaline mediums as described in the second patent. In both cases, the Co forms a stable complex compound, while the Ni breaks down, forming the hydroxide which may be removed; manganese complexes also are unstable.

1134. BRENNER, ABNER, AND RIDDELL, GRACE. Deposition of Nickel and Cobalt by Chemical Reduction. Nat. Bureau of Standards, Jour. Research, 1947, Research Paper 1835, pp. 385–395 (see Chem. Abs., vol. 41, 1947, p. 6513i); Chem. Abs., vol. 42, 1938, p. 1857g.

Additional data are presented on the deposition of Ni, Co, and Ni-Co alloys from hot hypophosphite solutions without the use of the electric current. The alkaline Ni solution, (pH 8–10) contains $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 30, $\text{NaH}_2\text{PO}_3 \cdot \text{H}_2\text{O}$ 10, NH_4Cl 50, and sodium citrate 100 gm. per l. A typical acid Ni solution (pH 4–6) contains $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 30, NaH_2PO_3 10, $\text{NaC}_2\text{H}_3\text{O}_2$ 50 gm. per l. A typical alkali Co solution (pH 9–10) contains $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ 30, $\text{NaH}_2\text{PO}_3 \cdot \text{H}_2\text{O}$ 20, and sodium citrate 100, NH_4Cl 50 gm. per l. The efficiency, in terms of the hypophosphite reacting, is 20 to 37 percent in the acid Ni solution and 66 percent in the acid Co solution. The reduction of metal takes place simultaneously on Fe, Ni, Au, Co, Al, Pd, and Zn and occasionally on Ag. Deposition can be obtained on noncatalytic surfaces by changing the composition of the bath, making contact with a more electronegative metal, or depositing a thin layer of a catalytic metal on the surface of the noncatalyst. Two possible mechanisms for the reaction are suggested.

1135. CLABAUGH, W. S., DONOVAN, J. W., AND GILCHRIST, R. Preparation of Nickel Chloride of High Purity. Nat. Bureau of Standards, Jour. Research, vol. 52, No. 2, February 1954, Research Paper 2475, pp. 73–74; Eng. Index, 1954, p. 712.

In developing methods of testing Ni salts used as analytical reagent-grade chemicals, it became necessary to prepare Ni compounds free of Co; the method consists of repeated precipitation by hydrogen chloride of nickel chloride dihydrate from a mixture of saturated aqueous solution of nickel chloride with acetone.

1136. DIEHL, HARVEY, AND LOHMAN, F. H. (Iowa State College, Ames). 5,8-Dihydroxyquinoline and Its Nickel Derivatives. Proc. Iowa Acad. Sci., vol. 61, pp. 255–259; Chem. Abs., vol. 49, 1955, p. 2929i.

5,8-Dihydroxyquinoline, which exhibits the combined properties of chelate ring formation and hydroquinone-quinone oxidation, has been examined, and its standard reduction potential and acid dissociation constant have been measured. It forms two Ni derivatives in which the ratios of organic compound to metal are 4:1 (precipitated below pH 6) and 2:1 (precipitated above pH 6). The Ni derivatives are somewhat too soluble to be useful for the gravimetric separation of Ni.

1137. DUBSKY, J. V., AND DOSTAL, V. [The Prepara-

tion of Cobalt Salts Free From Nickel Through the Cobalt Complexes.] Chem. Listy., vol. 26, 1932, pp. 593–595; Chem. Abs., vol. 27, 1933, p. 2900.

Cobalt salts (0.5 gm. in 2 cc. of H_2O) were decomposed by drops of a 75-percent KCN solution until the green precipitate redissolved, forming a green solution. The mixture was heated, treated with a few drops of H_2O_2 , and concentrated to a thick syrup. While still warm, crystalline dimethylglyoxime (0.1 gm.) was added and then 40 percent HCHO . An instantaneous precipitation of nickel dimethylglyoxime occurred. All certified pure cobalt salts gave a test for Ni, according to this procedure. Since the chemistry of preparing Co and Ni salts is very similar, uncontaminated salts can hardly be expected. Large differences in the chemical properties and reactions of Co and Ni occur in the complexes. A number of complexes including $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ were prepared and found to be free of Ni.

1138. DUISBURGER KUPFERHÜTTE. Separation of Iron, Cobalt, and Zinc From Solutions of Chlorinated, Roasted, Burned Pyrites. British Patent 729,001, Apr. 27, 1955; Chem. Abs., vol. 49, 1955, p. 13,064b.

The content of Fe, Co, and Zn of a solution of chlorinated, roasted, burned pyrites can be separated in stages by precipitating $\text{Fe}(\text{OH})_3$ with CaCO_3 at a pH of 3.5 to 4.0, precipitating $\text{Co}(\text{OH})_2$ with CaCO_3 or $\text{Zn}(\text{OH})_2$ at a pH of 3.7 to 4.2, and then precipitating $\text{Zn}(\text{OH})_2$ with $\text{Ca}(\text{OH})_2$ at a pH of 6.5 to 7.5. The precipitated slurry in each stage is thickened to a solids content of at least 800 gm. per l. and filtered in rotary filters.

1139. GARWIN, LEO, AND HIXSON, A. N. Separation of Nickel and Cobalt by Extraction From Aqueous Solution. Preliminary Studies. Ind. Eng. Chem., vol. 41, 1949, pp. 2298–2303; Chem. Abs., vol. 44, 1950, p. 497g.

Before a study of the separation of Ni and Co by liquid-liquid extraction, the solubilities of NiCl_2 and CoCl_2 were measured at 25° C. in various alcohols (butyl, amyl, iso-amyl, hexyl, iso-octyl, and capryl [2-octanol]), in ketones (methyl-ethyl, methyl-propyl, methyl iso-butyl, diethyl, diiso-propyl, and acetophenone), in ethyl acetate, isopropylacetate, isovaleric acid, BzH , furfural, Et_2O , isopropylether, heptane, benzene, MeNO_2 , PhNO_2 , PhCl , and $\text{ClCH}_2\text{CH}_2\text{Cl}$. Alcohols were the best solvents (dissolving more Co than Ni); hydrocarbons and aromatic compounds dissolved only traces. Capryl alcohol extracts little of either metal from H_2O solutions. Addition of HCl , CaCl_2 , NaCl , and NH_4Cl increased extraction while NaSO_4 suppressed it.

Effect of addition of electrolytes. Work cited above (pp. 2303–2310). Composition studies of 2 liquid-phase 5-component system— CoCl_2 , NiCl_2 , H_2O , capryl alcohol, and either HCl or CaCl_2 —at 25°, 50°, and 75° C. indicate that a process based on liquid-liquid extraction is feasible for the separation of the 2 metals.

1140. GEWERKSCHAFT SACHTLEBEN AND PÜTZER, HERMANN. [Potassium Nitrite—Separation of Ni and Co.] German Patent 472,605, Sept. 12, 1926; Chem. Abs., vol. 23, 1929, p. 3058°.

Potassium nitrite is recovered from Fischer's salt in the separation of Co and Ni in solution. The precipitate obtained is melted with caustic alkali and the CoO in the melt separated from the soluble part. Thus, a solution of CoSO_4 and NiSO_4 is mixed with KNO_3 and stirred. The precipitated potassium cobaltinitrite is filtered off, mixed with caustic alkali, and heated until it melts. The mass is treated with water and the CoO separated.

1141. ———. [Separating Cobalt and Nickel.] German Patent 484,241, May 5, 1927 (addition to Ger-

man Patent 472,605; Chem. Abs., vol. 23, 1929, p. 3058³); Chem. Abs., vol. 24, 1930, p. 1475.

Pure Ni-free $K_3Co(NO_2)_6$ is obtained by melting the precipitated salt with alkali hydroxide and extracting with water. The resulting solution of $K_3Co(NO_2)_6$ is virtually free of Ni.

1142. GORBUNOVA, K. M., AND NIKIFOROVA, A. A. (Institute of Physics and Chemistry, Academy of Sciences, U. S. S. R., Moscow). [Reduction of Nickel by Hypophosphite. Conditions of Formation and Several Properties of Layers.] Zhur. Fiz. Khim., vol. 28, 1954, pp. 883-896 (see Brenner and Riddell, Chem. Abs., vol. 42, 1948, p. 1857g); Chem. Abs., vol. 49, 1955, p. 6060h.

The rate of deposition (R) of Ni on metals from buffered aqueous solutions of $NiCl_2 \cdot 6H_2O$ and $NaH_2PO_4 \cdot H_2O$ was determined as a function of temperature (T), pH, concentrations of these two salts, nature and concentration of buffer, area of metal surface, and kind of metal, these parameters being varied one at a time. The conditions of reference were: Solution volume, 300 ml.; time, 1 hour; $T=90^\circ C$, $NiCl_2 \cdot 6H_2O$, 20 gm. per l.; $NaH_2PO_4 \cdot H_2O$, 10 gm. per l.; sodium glycolate 10 gm. per l.; pH 4-4.2; the metal 25 cm.² Armco Fe. The Ni deposits were photomicrographed. Data are detailed for results of varying the conditions, and a mechanism of reduction by hypophosphite suggested as occurring in two stages.

1143. GROTHE, HANS. [Separation of Nickel and Cobalt in Aqueous Solutions for the Practical Recovery of the Individual Metals.] Metall. u. Erz., vol. 30, 1933, pp. 449-455; Chem. Abs., vol. 28, 1934, p. 1309⁶.

If the original solution contains no more than 5 parts of Ni to 100 parts of Co, Co can be precipitated with $NH_4OH + (NH_4)_2SO_4$. The precipitate will contain no more than 1 part of Ni per 100 parts of Co.

1144. ———. [Separating Cobalt From Nickel.] German Patent 595,688, Apr. 20, 1934 (Cl. 40a 43.30); Chem. Abs., vol. 28, 1934, p. 5033⁴.

Solutions containing Ni and Co are treated with NH_3 in the proportion 2.25 molecules of NH_3 to 1 molecule of Ni-Co to precipitate the Co as a basic salt, the Ni being left in solution. Thus, a neutral solution containing sulfates of Ni and Co is treated with $(NH_4)_2SO_4$ and warmed. The Co is precipitated and filtered off. The precipitate is dissolved in H_2SO_4 , neutralized with NaOH, and treated with NH_3 . The precipitate contains Co and traces of Ni. The filtrate is boiled and refiltered. The resulting filtrate contains Ni and only traces of Co.

1145. HEINERT, ERICH. [Basic Nickel Carbonate.] German Patent 761,584, Jan. 19, 1953 (Cl. 12n 4). Chem. Abs., vol. 49, 1955, p. 3488f.

Aqueous solutions of Co-containing nickel salts are treated with aqueous NH_3 in a quantity insufficient to cause precipitation. Enough alkali metal carbonate to precipitate all of the Ni as basic nickel carbonate is then added. Ammonia is removed by bubbling air or a similar inert gas or gas mixture through the solution, possibly with heating. The process yields basic nickel carbonate free of Co, which latter remains dissolved as ammino complex. Thus, 100 parts N nickel sulfate solution (1.8 parts Co/100 parts Ni) is poured with stirring into 70 parts by volume of concentrated NH_4OH , d. 0.91. Normal Na_2CO_3 solution (100 parts) is then added and NH_3 is expelled by introduction of a finely dispersed stream of air. Pale green, readily filterable basic nickel carbonate is precipitated, separated, washed, and dried.

1146. IPAT'EV, V. N., AND MUROMTSEV, B. [Displacement of Metals and Their Oxides From Solution of Their Salts by Hydrogen at High Temperatures and Pressures.] Ber. Deut. chem. Gesell., vol. 63B, 1930,

pp. 160-166 (see following abs.); Chem. Abs., vol. 24, 1930, p. 2074².

As a result of the reduction of the anion, it is possible to convert the nitrates of metals in solution into the corresponding oxides, and a few may even be reduced to the free metal by H_2 at 250 atmospheres of pressure and 200° - $300^\circ C$. The products formed depend somewhat on the character of the material of which the retaining bomb is constructed.

1147. KNOCHE, HEDWIG. [The "Induced" Solubility of Ferric Hydroxide and Several Other Hydroxides in Caustic Solutions in the Presence of Chromium Hydroxide. III.] Kolloid-Ztschr., vol. 68, 1934, pp. 37-41 (see Chem. Abs., vol. 28, 1934, p. 4960¹); Chem. Abs., vol. 28, 1934, p. 6359⁵.

Bivalent Co, Cu, Mn, Ni, Cd, Mg, and trivalent thallium hydroxides show an induced solubility in alkali solutions in the presence of Cr. Co, Ni, and Mg solutions with Cr become turbid rapidly; Fe, Ti, Cu, Cd, and Mn remain clear, showing some chromate formation. In all cases, KOH has a higher dissolving power than NaOH on account of the aging effect of NaOH and NaCl. Fe and Ti hydroxides have the highest solubility and are the only ones with solubility products smaller than that of $Cr(OH)_3$. Dilute $Cr(OH)_3$ solutions peptize Fe, Ti, Mn, Cu, and Co hydroxides but not Mg, Co, and Ni hydroxides. Al and Zn hydroxides are neither dissolved nor peptized by caustic $Cr(OH)_3$ liquors.

1148. KYLANDER, R. L., AND GARWIN, LEO (Continental Oil, Ponca City, Okla.). Extraction of Cobaltous Chloride With Capryl Alcohol in a Spray Tower. Chem. Eng. Progress, vol. 47, 1951, pp. 186-190; Chem. Abs., vol. 45, 1951, p. 4493g.

Because of the similar properties of Ni and Co, their separation has presented considerable difficulty to the metallurgical industry. At present, the most widely used processes involve the precipitation of the Co in the form of the hydrated cobaltic oxide ($Co_2O_3 \cdot 3H_2O$) by the addition of an alkaline solution of an oxidizing agent to an acid solution of the bivalent salts. Garwin and Hixson (Chem. Abs., vol. 44, 1950, p. 197i) have carried out a systematic investigation of the possibility of separating the chlorides of Ni and Co by selective extraction with an organic solvent. Capryl alcohol was found to be an effective selective solvent for cobalt chloride in the presence of considerable HCl or CaCl in the water phase. Using a spray tower, the ratio of Co to Ni in the extract averaged in the range of 200 to 1. This was obtained from about 1.3:1 ratio of the metals in the salts, showing that considerable separation of these two salts can be obtained in an extraction tower operated under steady-state conditions.

1149. LENANDER, N. E. (assigned to Orkla Grube-Aktiebolag). Separating Cobalt and Iron From Solutions Such as Those Obtained by Lixiviating Roasted Pyrites. U. S. Patent 1,783,046, Nov. 25, 1931; Chem. Abs., vol. 25, 1931, p. 274².

Ferrous Fe in the solution is oxidized with an alkali metal chlorate, the ferric Fe is precipitated, and the Co is then recovered from the solution.

1150. MOORE, T. E., LARAN, R. J., AND YATES, P. C. (Oklahoma Agricultural and Mechanical College, Stillwater). Extraction of Inorganic Salts by 2-Octanol. I. Cobalt (II) and Nickel (II) Perchlorates. Jour. Phys. Chem., vol. 59, 1955, pp. 90-91 (see Chem. Abs., vol. 48, 1954, p. 1874i); Chem. Abs., vol. 49, 1955, p. 4378b.

The distribution coefficients of these salts were almost alike at $30^\circ C$. and were much higher than those of the corresponding chlorides. The extraction of $Co(ClO_4)_2$ at constant initial aqueous concentration

was studied in the presence of varying concentrations of LiClO_4 , $\text{Ca}(\text{ClO}_4)_2$, and $\text{Al}(\text{ClO}_4)_3$. Their influence was due primarily to the mass-action effect of the perchlorate ions. The ratio of the 2-octanol and aqueous phase activities of $\text{Co}(\text{ClO}_4)_2$ in mixed extractions with $\text{Ca}(\text{ClO}_4)_2$ were calculated by making assumptions regarding the activity coefficients in each phase. The differences in the chloride-promoted 2-octanol extractions of CoCl_2 and NiCl_2 are not the result of differences in the extraction behavior of Ni and Co ions but arise from specific promoting salt-transition metal salt interactions.

1151. MORGAN, G. T., AND MAINSMITH, J. D. Separation of Cobalt From Nickelferous Ores by the Purpureo-Cobalt Chloride Process. *Jour. Soc. Chem. Ind.*, vol. 43, 1924, pp. 131-133-T; Bureau of Mines Inf. Circ. 6331, 1930, p. 32.

1152. ORKLA GRUBE-AKTIEBOLAG. Separating Iron From Solutions Containing Also Cobalt. British Patent 329,543, June 18, 1929; *Chem. Abs.*, vol. 24, 1930, p. 5711⁵.

Solutions containing Co, much Fe, and possibly also Zn and Cu from the lixiviation of chlorinated roasted pyrite are treated with a chlorate, preferably NaClO_3 . This addition may be made after first introducing scrap-Fe to precipitate Cu, and after removing Na_2SO_4 by cooling to 10°C . The Fe is accordingly oxidized at a temperature of 60°C ., precipitated by the addition of an aqueous lime suspension, and removed. The filtrate may be further treated for recovery of Co, Zn, etc. (*see Chem. Abs.*, vol. 24, 1930, p. 2845).

1153. ———. [Cobalt.] French Patent 676,234, June 5, 1929; *Chem. Abs.*, vol. 24, 1930, p. 2845¹.

In the separation of Co from solutions rich in Fe—for example, those obtained after Cu and Na_2SO_4 have been removed from solutions resulting from the lixiviation of roasted pyrites—the Fe is oxidized by alkali perchlorates, particularly NaClO_4 .

1154. OSTROUMOV, E. A. [Separation of Iron, Aluminum, and Chromium From Manganese, Cobalt, Nickel With Pyridine.] *Ztschr. anal. Chem.*, vol. 106, 1936, pp. 170-176; *British Chem. Abs.*, 1936, p. A-1222.

Precipitation of Fe, Cr, and Al as hydroxides from dilute HCl or HNO_3 solution by means of 20 percent aqueous $\text{C}_2\text{H}_5\text{N}$ at 60° - 70°C ., in the presence of NH_4Cl or NH_4NO_3 , affords a quantitative separation from Mn, Co, and Ni with one precipitation. Large amounts of SO_4^{--} should not be present.

1155. RAYMOND, E. [Quantitative Separation of Nickel and Cobalt.] *Compt. rend.*, vol. 200, 1935, pp. 1850-1852; *British Chem. Abs.*, 1935, p. A-951.

To the solution of Ni and Co salts is added an excess of 20 percent $\text{N}(\text{CH}_3\text{CH}_2\text{OH})_3$, and then excess of aqueous NaOH. Both metals form complex salts, that of Ni being decomposed quantitatively by boiling, with precipitation of $\text{Ni}(\text{OH})_2$.

1156. RIGAMONTI, R., AND SPACCAMELA-MARCHETTI, E. University of Turin, Italy). [Separation of Metallic Salts by Means of Countercurrent Liquid-Liquid Extraction. I. Nickel-Cobalt.] *Chimica e industria*, Milan, vol. 36, 1954, pp. 91-98 (*see Garwin and Hixson, Chem. Abs.*, vol. 44, 1950, p. 497gi); *Chem. Abs.*, vol. 48, 1954, p. 7485h.

Preliminary work on the separation of the acetates of Co and Ni in the 2-phase system H_2O - MeOH - BuOH (10:40:50) at 25°C . proved unsatisfactory; ratios of distribution coefficients, $K(\text{Co})/K(\text{Ni})$, were approximately unity, indicating low selectivity. In further studies, the method of Rosenheim and Huldchinsky (*Ber. deut. chem. Gesell.* vol. 34, 1901, p. 2050) was adapted to the use of H_2O - AmOH to effect selective separation of Co and Ni as complexes of SCN^- . By varying ratios of $\text{SCN}/\text{Co}+\text{Ni}$ from 1 to 24 with addi-

tion of NH_4SCN in excess, values of $K(\text{Co})$, $K(\text{Ni})$, and $K(\text{Co})/K(\text{Ni})$ ranged from 0.14 to 2.68, 0.18 to 0.5, and 0.85 to 5.20, respectively. With the use of standard equations for countercurrent extraction, for example, Treybald (*Chem. Abs.*, vol. 45, 1951, p. 4101i), assuming $\text{SCN}^-/(\text{Co}+\text{Ni})=12$, $K(\text{Ni})=0.4335$, and $K(\text{Co})=2.128$, made a calculation indicating 99.9-percent separation with 17-19 plates. Experimental proof with laboratory equipment with 7 plates yielded results only slightly lower than the value computed for that number (about 90 percent). Variations of the $K(\text{Co})$ coefficient as a function of the concentration of the SCN^- ions confirmed the existence of the complex $\text{Co}(\text{SCN})_{4+2}$; Ni formed only $\text{Ni}(\text{SCN})_2$. Numerous data are tabulated and plotted (20 refs.).

1157. ROSENDAHL, RICHARD. [Separation of Cobalt From Manganese.] German Patent 568,643, June 29, 1928; *Chem. Abs.*, vol. 27, 1933, p. 2769.

Cobalt slurry is treated with an equivalent amount of a reducing agent such as FeCl_2 , FeSO_4 , CuCl , $\text{SO}_2(\text{CO}_2\text{H})_2$, etc., to yield soluble Co compounds for separation from the Mn present.

1158. ———. [Cobalt.] German Patent 579,554, June 28, 1933; *Chem. Abs.*, vol. 28, 1934, p. 1008⁹.

In working up Co slurry, the Zn contained is first dissolved with a hot zinc salt solution, and the Co is then extracted by treatment with cold acid. The Zn_2OCl_2 of the first process is precipitated by the addition of acid.

1159. ———. [Cobalt.] German Patent 585,368, Oct. 6, 1933; *Chem. Abs.*, vol. 28, 1934, p. 1320⁹.

An aqueous sludge containing $\text{Co}(\text{OH})_2$, a higher hydroxide of Mn, and hydroxides of Zn, Ni, and Cu are treated with an aqueous solution of a ferric or cupric salt, in an excess of 20 to 50 percent over the amount that is equivalent to the hydroxides of Zn, Ni, and Cu present. The latter hydroxides are thus dissolved. The residue containing $\text{Co}(\text{OH})_2$ and hydroxide of Mn is treated with a reducing agent (for example, FeCl_2 or SO_2) to produce a solution containing Co and Mn, from which the metals are separated in known manner.

1160. SCHAUFELBERGER, F. A. (assigned to Chemical Construction Corp.). Separation of Cobalt as Carbonates From Nickel-Cobalt Mixtures. U. S. Patent 2,711,957, June 28, 1955; *Chem. Abs.*, vol. 49, 1955, p. 12,260i.

The solution containing Co and Ni is treated by adjustment of the carbonate content to precipitate only as much of the cobalt carbonate as will precipitate in the Ni-free state. This precipitate is removed and the residual solution treated to precipitate the rest of the Co by adjustment of the $(\text{NH}_4)_2\text{CO}_3$ content, followed by heating. The impure Co precipitate is collected and the resultant Co-free Ni solution passed to a Ni recovery system. (*See preceding and following abstracts.*)

1161. SCHAUFELBERGER, F. A., AND DASHER, J. O. (assigned to Chemical Construction Corp.). Separation of Nickel From Cobalt-Nickel Salt Solutions. U. S. Patent 2,711,958, June 28, 1955; *Chem. Abs.*, vol. 49, 1955, p. 12,261b.

A solution or slurry having a Ni:Co ratio of less than 1 is adjusted to contain NH_3 and ammonium salts in concentrations at which all of the Ni and all of the Co not present as carbonate are in a state of dissolution. By proper adjustment of the carbonate content, precipitation of cobalt carbonate increases the dissolved Ni:Co mole ratio to at least 1, preferably higher. The precipitate is removed and the residual solution adjusted to provide a concentration of NH_3 , ammonium salts, and carbonate suitable for recovery of Ni by reduction. The Ni powder is filtered

and washed, and the filtrate and washings recycled for recovery of residual Ni.

1162. SMITH, S. C. Treating Cobalt Solutions. British Patent 298,301, July 25, 1927; Chem. Abs., vol. 23, 1929, p. 2790².

Solutions containing a Co salt, such as the sulfate, are treated with PbO_2 in the presence of a soluble Ni compound. The Co and Pb together form a precipitate that is separated and leached with H_2SO_4 to dissolve the Co. The residue is reconverted into PbO_2 for further use. The process may be used for separating Co and Ni from solutions obtained from the ores.

1163. SPACU, P. [Quantitative Separation of Iron and Cobalt.] Compt. rend., vol. 200, 1935, pp. 1595-1597; British Chem. Abs., 1935, p. A-838.

Treatment of a hot solution containing Fe^{++} and Co^{++} with C_2H_5N separates all the Fe as $Fe(OH)_3$, while the Co remains in solution.

1164. TILU, M. M. Separation of Cobalt From Nickel Using Acetone as a Solvent. Jour. Indian Chem. Soc., vol. 20, 1943, pp. 139-140; Chem. Abs., vol. 38, 1944, p. 313².

The solubility of $NiCl_2 \cdot 6H_2O$ in acetone is extremely slight, 1 part of the salt in 16,000 parts of acetone at 35° C., but $CoCl_2 \cdot 6H_2O$ is very soluble. In experiments on separation of Co and Ni by means of this difference in solubility there were slight losses of Co and Ni. The Co loss was of the order of 0.4-1.0 mg. with Co to Ni ratios 0.0656 to 0.3540 and 0.2652 to 0.0838. The Ni loss varied from +0.3 to -1.0 mg.

PURIFICATION OF MATERIALS FOR ELECTROLYSIS

1165. CHAYBANY, A. Imperfections in Electrodeposits. The Electrodeposition of Cobalt. Metal Ind. (London), vol. 47, 1935, pp. 423-426; Met. Abs. (in Metals and Alloys), vol. 7, p. 356; Chem. Abs., vol. 31, 1937, p. 4212².

An attempt was made to determine the causes of pores and pinholes in electrodeposits for the purpose of suppressing their formation. From experiments with neutral solutions and acidifications with H_2SO_4 , HCl, and HF, it was concluded that pores and pinholes were caused by impurities present in the cobalt salt. Ni, Fe, Cu, Pb, and As were present in small amount. A special study was made of the effects of feeble concentrations of As, and Chaybany traces the imperfections to this element.

1166. CHURCHWARD, R. E., AND SHELTON, F. K. Cobalt Solution Purification. U. S. Patent 2,476,284, July 19, 1949; Chem. Abs., vol. 43, 1949, p. 8107f.

A process is described for purification of Co compounds suitable for metallic Co electro-winning purposes. To an impure Co salt solution having a pH 4-5 is added enough Cu or Fe to lie in the range of 0.1 to 10 gm. per liter of each. The solution is treated with an excess of H_2S at about 20 p. s. i. followed by the separation of the precipitant. The acidity of the solution is then adjusted to pH 5 to 6, air passed through the solution at 50°-60° C., and the precipitate formed is removed.

1167. CHURCHWARD, R. E., SHELTON, F. K., AND KNICKERBOCKER, R. G. Impurities in the Electro-winning of Cobalt. Trans. Electrochem. Soc., vol. 25, 1944, 20 pp. (preprint); Chem. Abs., vol. 38, 1944, p. 2272².

In electrolyzing a standard fluoroborate electrolyte containing 20 gm. per l. Co as $CoSO_4$, 50 gm. per l. boric acid, and 5 gm. per l. NaF at 25 a. per sq. ft., using Pb

anodes and stainless steel cathodes, the maximum tolerance for the metallic impurities for the production of 7-hour Co electrodeposits is (in mg. per l.) Zn 10, Cd 1, As^{+++} 3, As^{+} 1, Sb^{+++} 10, and Hg^{++} 1. Trivalent and hexavalent Cr in concentrations up to 100 m. per l. were only slightly harmful, while Ni, Cu, Fe, and Mg were not found deleterious. The impurities can be removed by: (1) Recrystallization of $CoSO_4$, (2) recrystallization of $CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, or (3) precipitation of the impurities with H_2S under 20 p. s. i. at a pH 4.0, followed by the familiar Fe purification.

1168. EWING, D. T., WERNER, J. K., OWEN, C. J., DOW, W. O., AND ROWE, R. J. (Michigan State College, East Lansing, Mich.). Effect of Impurities and Purification of Electroplating Solutions. 1. Nickel Solutions. 8. The Effects and Removal of Lead. AES Research Project 5. Plating, vol. 41, 1954, pp. 1307-1311 (see Chem. Abs., vol. 48, 1954, p. 5002h); Chem. Abs., vol. 49, 1955, p. 5162f.

Lead impurity up to 35 mg. per l. tended to brighten deposits slightly and increase salt-spray resistance slightly. The effect of other impurities was slight. Lead can be removed to 2.5 mg. per l. by low current-density electrolysis (1 a. per sq. ft.) or by precipitation at pH 5.8.

1169. FALCONBRIDGE NICKEL MINES, LTD. Electrolytic Recovery of Nickel. British Patent 667,659, Mar. 5, 1952; Chem. Abs., vol. 46, 1952, p. 6974c.

In the production of high-purity Ni with the recovery of Co and Cu, the Fe, Co, Cu, Pb, and As are removed from the $NiSO_4-NiCl_2$ electrolyte by oxidation with chlorine and precipitation as hydroxides. A portion of the electrolyte is withdrawn regularly and electrolyzed to remove excess chlorine and H_2SO_4 , and, thereby to maintain the desirable conditions for deposition of Ni; both chlorine and H_2SO_4 are reused, the former to precipitate Co and other metals and to produce HCl, and the latter to produce fresh $NiSO_4$ for controlling the Ni content of the system. Cu may be removed by cementation and Fe by aeration before treatment with chlorine.

1170. FALCONBRIDGE NIKKELVERK AKTIESELSKAP. [Purification of Nickel Electrolytes.] Norwegian Patent 54,689, Dec. 10, 1934; Chem. Abs., vol. 29, 1935, p. 5755².

After the ordinary purification, the electrolysis solution is treated in a separate electrolysis to free it from impurities of Cu, Fe, As, and Pb, which are more easily precipitated than Ni due to their position in the electromotive series, migration velocity of ions, overvoltage, or other electrochemical properties.

1171. FEDOT'EV, N. Extraction of Pure Metal (Cobalt) by Electrolysis. Metal Ind. (London), vol. 67, 1945, p. 200; British Abs., 1947, p. B-1-191.

To the electrolyte containing $CoSO_4$ and H_2SO_4 , basic cobalt carbonate is added continuously to maintain the cobalt concentration during electrodeposition of the metal. The anode is ferrosilicon (13 percent Si), and the Fe cathode is enclosed in a diaphragm bag to prevent Fe from entering the solution. Ni is eliminated before electrolysis by means of a suspension of solid dimethylglyoxime, excess of the latter being adsorbed on activated C. The Co deposit contains 0.02 percent of Fe and 0.05 percent of Ni.

1172. FEDOT'EV, N. P., AND SVECHNIKOVA, V. V. [Electrochemical Oxidation of Nickel Monoxide Hydrate.] Jour. Appl. Chem., U. S. S. R., vol. 15, 1942, pp. 105-119; Chem. Abs., vol. 37, 1943, p. 2274¹.

The commercial possibility of an electrochemical method for the preparation of black nickel oxide hydrate, which is suitable for clean-up of Ni electrolyte, was studied. Green NiO hydrate was oxidized at

graphite anodes in NaCl solution; or NaCl solution was electrolyzed with graphite and Ni anodes. The first procedure appeared more practical economically. For best results, use 5 N NaCl with 0.025 NaOH, temperature 20° C., anode current density 0.1 to 1.0 a. per cm.²; this yields the black hydrate.

1173. FINK, C. G., AND ROHRMAN, F. A. The Preparation of Pure Electrolytic Nickel. II. The Final Elimination of Copper and the Removal of Cobalt and Iron. *Trans. Am. Electrochem. Soc.*, vol. 58, 1930, 18 pp. (preprint) (*see Chem. Abs.*, vol. 24, 1930, p. 1299); *Chem. Abs.*, vol. 24, 1930, p. 4715⁷.

1174. ———. The Preparation of Pure Electrolytic Nickel. I. The Elimination of Copper From Nickel-Copper Electrolytes. *Trans. Am. Electrochem. Soc.*, vol. 57, 1930, 13 pp. (preprint 2); *Chem. Abs.*, vol. 24, 1930, p. 1290⁷.

The separation of Cu from Ni has been difficult and has been the subject of investigation for many years. Electrochemical methods, using aqueous solutions, were investigated by Fink and Rohrman and the effects of pH and other factors studied. High acidity, low current density, high temperature, and vigorous circulation favor the deposition and removal of Cu. A rapid method for removing Cu from Ni solutions is presented.

1175. GRONNINGSÆTER, A. M. Electrodeposition of Nickel. U. S. Patent 2,066,347, Jan. 5, 1937. *Chem. Abs.*, vol. 31, 1937, p. 954⁵.

An impure Ni electrolyte contaminated with an objectionable content of Cu, Fe, As, Pb, etc., is first subjected to Cu cementation on gas-reduced Ni and to Fe precipitation by oxidation to remove most of the Cu and Fe and to render the electrolyte substantially neutral. At least one preliminary electrolysis is performed with a soluble Ni anode with rapid movement between electrolyte and cathode to deposit most of the impurities together with a small amount of Ni. Following this, the main electrolysis is ready to be done in a separate operation.

1176. GRONNINGSÆTER, A. M., AND HOMMEREN, B. G. (assigned to Falconbridge Nickel Mines, Ltd.). Purification of Nickel Electrolyte. Canadian Patent 400,642, Nov. 11, 1941; *Chem. Abs.*, vol. 36, 1942, p. 1551⁶.

Ni electrolyte containing only small amounts of impurities (for example, Pb, As, and Cu) is treated with Fe(OH)₃, prepared by wet precipitation to adsorb a substantial amount of impurities. The electrolyte is not acid enough to dissolve the Fe(OH)₃. The apparatus is described.

1177. ——— (assigned to Falconbridge Nickel Mines, Ltd.). Electrolytic Refining of Nickel. U. S. Patent 2,450,426, Oct. 5, 1948; *Chem. Abs.*, vol. 43, 1949, p. 1665e.

Ni electrolyte (I) is purified by the use of Fe(OH)₃ (II). The Fe in the Ni anode is controlled to limit the Fe content of (I) to 0.3 to 0.4 percent. This Fe which precipitated during aeration, carries with it adsorbed As, Pb, and Cu. The refiltered (I) is then used for the electrolytic production of Ni.

1178. GUTMAN, M. I., AND MAYANTZ, A. D. [Freeing Nickel Sulfate Solutions From Iron and Aluminum Impurities.] *Tsvetnye Metal*, No. 6, 1934, pp. 63-71; *Chem. Abs.*, vol. 29, 1935, p. 4527⁴.

Solutions obtained by leaching the roasted mixture of nickel, iron, and aluminum sulfates contain 1 to 2 parts of Fe plus Al to 1 part of Ni. Calcium or magnesium carbonates were used to precipitate Fe and Al; it was found preferable to oxidize Fe by air treatment rather than to introduce manganese dioxide, and to use magnesium carbonate as the precipitant.

1179. KOBYLIN, P. A. [Purification of Nickel-Salt Solutions.] Russian Patent 36,412, May 31, 1934; *Chem. Abs.*, vol. 32, 1938, p. 3560⁷.

Fe salts are precipitated from the Ni salt solutions by treatment with nickel hydroxide.

1180. MATTACOTTI, V. Purification of Nickel Solutions by Electrolysis. *Monthly Rev. Am. Electroplaters' Soc.*, vol. 25, 1938, pp. 513-520; *Chem. Abs.*, vol. 32, 1938, p. 6952⁶.

Small quantities of impurities may cause electroplating baths to give poor results. A simple test is to bend the cathode, and plate on it; if impurities are present, a dark ellipse will form inside the bend where the current is low. Remedies are (1) removal of Fe as Fe(OH)₃; (2) addition of H₂O₂; (3) treatment with activated carbon; and (4) electrolysis. Conditions for removal of impurities by electrolysis are detailed.

1181. MIKI, HIDETO (Onoda Technical High School). [Purification of Impure Nickel Electrolyte by a Sulfide Method. I. Calcium Polysulfide as Precipitating Agent.] *Jour. Chem. Soc., Japan, Ind. Chem. Sec.*, vol. 54, 1951, pp. 361-363; *Chem. Abs.*, vol. 47, 1953, p. 5276i.

The addition of calcium polysulfide containing CaS₂O₃ to the anolyte of a Ni electrolyte precipitates impurities such as Cu and As as sulfides, while Ni remains in solution. The smaller the amount of CaS₂O₃, the better the separation.

1182. MUKAI, MASAO, AND TAKEI, TAKESHI. [Separation of Iron From Nickel by Alternating Current.] *Jour. Electrochem. Soc., Japan*, vol. 15, 1947, pp. 30-32; *Chem. Abs.*, vol. 44, 1950, p. 9832c.

With an alternating current Fe²⁺ alone is electrolytically oxidized and precipitated from a solution containing Fe²⁺ and Ni²⁺ with a current efficiency of 25 to 30 percent. The optimum conditions are: Electrolyte solution, dilute H₂SO₄ and NaNO₃ (3 to 5 percent); electrode Pb or its alloys; current density 20 to 25 a. per dm.²; time of electrolysis, 1 to 2 hr.; temperature, 50° C.; and bath voltage, 25 to 30 v. The commercial use of this method is difficult because of the low current efficiency and large electrode consumption, (20 mg. per a.-hr.).

1183. PAL'GUEV, S. F., SMIRNOV, M. V., AND KARPACHEV, S. V. Dependence of the Quality of Cathodic Nickel Deposits on the Presence of Impurities in the Electrolyte. *Jour. Appl. Chem., U. S. S. R.*, vol. 26, 1953, pp. 45-48 (English trans.) (*see Chem. Abs.*, vol. 47, 1953, p. 6794i); *Chem. Abs.*, vol. 49, 1955, p. 2903f.

1184. ———. [Dependence of the Quality of Cathodic Nickel Deposits on the Presence of Impurities in the Electrolyte.] *Chem.-Met. Inst. Ural Branch Acad. Sci., U. S. S. R., Sverdlovsk. Zhur. Priklady Khim.*, vol. 26, 1953, pp. 50-54; *Chem. Abs.*, vol. 47, 1953, p. 6794i.

Electrolysis of 0.2 to 1.0 percent nickel chloride in a fused equimolecular mixture of sodium chloride and potassium chloride, at 700°-750° C. with a current density of 0.015 to 0.06 a. per cm.² gives unsatisfactory dendritic deposits. The quality of the deposit is improved after a 24-hour purification of the electrolyte with a dry HCl gas stream. This treatment gives rise to adherent Ni deposits, apparently eliminating a green nickel oxide film. Compact deposits 0.13 to 0.14 mm. thick can be obtained.

1185. PALMAER, K. W. Electrolytic Removal of Iron-Group Metals From Solutions Such as Those of Aluminum Salts. U. S. Patent 1,900,996, Mar. 14, 1933 (*see German Patent 545,130*, *Chem. Abs.*, vol. 26, 1932, p. 2929); *Chem. Abs.*, vol. 27, 1933, p. 2888².

1186. PALMAER, K. W., AND GRIEF, O. E. Electrolytic Removal of Metals of the Iron Group From Solutions. U. S. Patent 1,970,974, Aug. 21, 1934 (*see Chem. Abs.*,

vol. 26, 1932, p. 2929); Chem. Abs., vol. 28, 1934, p. 6070⁷.

In an operation using a Hg cathode, the contaminated Hg is removed from the cell, metals taken up by the Hg in the electrolyzing process are removed from it by use of a purifying agent such as a ferric salt, and the purified Hg is returned to the cell. In the purification a quantity of the purifying agent is used which is less than the chemical equivalent to the contaminating metal present in the Hg, so that only a portion of the contaminating metal is removed. The apparatus is described. United States Patent 1,970,975 relates to operative details of a process for electrodeposition of metals such as those of the Fe group from solutions of their salts by use of a cathode of Hg flowing over a vertical or inclined support. The apparatus is described.

1187. PEEK, R. L., AND KNITTEL, C. A. (assigned to International Nickel Co.). Treating Nickel-Bearing Solutions Contaminated With Copper and Iron. U. S. Patent 1,887,037, Nov. 8, 1933; Chem. Abs., vol. 27, 1933, p. 1311.

The solution is treated with a metal powder consisting mainly of Ni, obtained by a low-temperature gas reduction. Cementation of the dissolved Cu and reduction of the H-ion concentration to a point (pH 5.6) where any Fe in the solution will be precipitated solely by aeration are accomplished by sufficient addition of this powder. The product is a purified solution suitable for the electrodeposition of Ni.

1188. PESIN, Y. M., ANDREEVA, O. I., MORENO, A. A., AND SCHIMANZAR, M. P. [Purifying Nickel Electrolyte.] Russian Patent 57,817, Aug. 31, 1940; Chem. Abs., vol. 38, 1944, p. 5156⁸.

The Ni solution is treated at 80° C. with Ni(OH)₂, in a quantity equivalent to the Fe present, the hydrated ferric oxide formed is removed, and the solution is treated with a further quantity of Ni(OH)₂ to remove Co.

1189. ———. [Fractional Purification of Nickel Electrolytes for the Removal of Iron and Cobalt, Formation of "Black Hydrate" of Nickel.] Tsvetnye Metal, vol. 16, No. 8, 1941, pp. 29–35; Chem. Abs., vol. 38, 1944, p. 3918⁸.

With NaClO and NiSO₄ in the presence of NaOH the reactions $\text{Ni(OH)}_2 + \text{NaClO} + \text{H}_2\text{O} = \text{Ni(OH)}_3 + \text{NaCl}$ and $\text{NiSO}_4 + 2\text{NaOH} = \text{Ni(OH)}_2 + \text{Na}_2\text{SO}_4$ occur. Increasing the amount of NaClO from 0.5 to 2.0 equivalents, calculated on the NiO₂ content, increased the active oxygen in the black hydrate. Further increase in the amount added had no effect. At temperatures above 60° C., NaClO and NaOH had to be added carefully to prevent violent reaction. Increasing the amount of alkali at constant hypochlorite concentration increased the amount of O₂ in the black hydrate; thus at 1.15 equivalents of NaOH the product was NiO_{1.44}, and at 10 equivalents NiO_{1.76}. Slow addition of NaClO increased the utilization coefficient. Na₂CO₃

produced lower active O₂ in the hydrate. Optimum conditions for obtaining the black hydrate are: Hypochlorite 1.5 equivalents (calculated on NiO₂), NaOH 1.1 equivalents, room temperature, and fractional addition of hypochlorite.

1190. SERGEEV, M. [The Purification of Regenerated Nickel Sulfate.] Masloboino Zhirovoe Delo, No. 3, 1929, pp. 57–62; Chem. Abs., vol. 24, 1930, p. 6045.

Solutions of NiSO₄, regenerated from hydrogenation catalysts, are purified by means of CuSO₄ and Na₂CO₃.

1191. SHCHERBAKOV, I. G., LOSHKAREV, M. A., AND LOSHKAREV, A. F. [Effect of Organic Impurities in the Electrolyte Used in Refining Nickel.] Tsvetnye Metal, No. 9, 1939, pp. 77–84; Chem. Abs., vol. 35, 1941, p. 33⁷.

Various organics likely to be present in the bath cause slow depolarization and slow deposition of Ni and may result in completion of deposition in one facet of crystals in the lattice before the next layer is started. Methods for cleaning diaphragm mediums and removal of foreign organics by oxidation or entrainment in activated charcoal are discussed.

1192. SHELTON, F. K. Purification of Cobalt. U. S. Patent Appl. 58,021; Official Gazetteer 661,307, 1952; Chem. Abs., vol. 47, 1953, p. 10,450f.

Ores, concentrates, or precipitates of Co are first leached with an alkali compound to remove As and Zn, then treated with H₂SO₄, dissolving out Co and Fe; then a controlled pH of 5.4 attained by addition of caustic soda precipitates Fe. A solution suitable for electrowinning the Co is obtained upon removal of the precipitate. Caustic soda is regenerated and recycled. Zn and As are also recovered.

1193. VON WURSTEMBERGER, FRANZ. [Purification of Nickel Electrolytic Baths.] Swiss Patent 131,827, Apr. 12, 1928; Chem. Abs., vol. 23, 1929, p. 4898⁷.

Ni baths are cleared of foreign metals, especially Cu, by interpolating a different current at intervals in the electrolysis.

1194. WEISBERG, LOUIS. Purifying Nickel-Plating Solutions by Electrolysis. Metal Ind. (N. Y.), vol. 35, 1937, pp. 451–453; Chem. Abs., vol. 32, 1938, p. 5705⁷.

Removal of metallic and some types of organic impurities from these solutions by electrolysis at a regulated current density is discussed.

1195. ZAKHAROVA, G., MISHUROVA, M., BAUMAN, M., AND GOLENDEEV, V. [Purifying Nickel Sulfate Solutions by Oxidizing Iron With Air.] Trudni VNIIZh, No. 3, 1934, pp. 30–36; Chem. Abs., vol. 29, 1935, p. 8245⁷.

In removing Fe from nickel sulfate solutions, the commercial method using dry soda ash and oxidizing at 80°–90° C. is less efficient than air oxidation at 50°–60° C. with not over 10 percent excess of soda ash. The oxidation is facilitated by the presence of phosphoric acid.

PART IV. ELECTROMETALLURGICAL ELECTROMETALLURGY

1196. ALTERTHUM, H. [The Production and Uses of Nonferrous Metals in Electrotechnology. III. Nickel and Nickel Alloys.] *Metallwirtschaft*, vol. 7, pp. 728-731; *Chem. Abs.*, vol. 23, 1929, p. 3198.

1197. CENTER, A. A. *Electrometallurgy*. *Eng. and Min. Jour.*, vol. 143, No. 2, February 1942, pp. 93-94; *Eng. Index*, 1942, p. 391.

The electrometallurgy of metals, including Ni and Co, is discussed.

1198. CUTHBERTSON, J. W. (Tin Research Institute, Greenford, England). Recent Advances in the Electrolytic Extraction of Manganese, Chromium, and Cobalt. *Chem. and Ind.*, 1952, pp. 1165-1170 (21 refs.); *Chem. Abs.*, vol. 47, 1953, p. 2064c.

1199. DENNIS, W. H. Recovery of Metals by Electricity. A Short Review of Its Applications. *Mine and Quarry Eng.*, vol. 36, 1947, pp. 75-82; *Chem. Abs.*, vol. 41, 1947, p. 5801g; *Eng. Index*, 1947, p. 784.

General applications of electrolytic processes are presented, including also the recovery of Cu, Pb, Ni, and precious metals using soluble anodes, and of Al, Mg, Mn, Zn, and Cd with insoluble anodes.

1200. DONAHUE, T. H. Status of Electrolysis As a Metallurgical Process. *Trans. Am. Electrochem. Soc.*, vol. 57, 1930 preprint, 20 pp.; *Chem. Abs.*, vol. 24, 1930, p. 2953^o.

Through introduction of electrolytic methods and flotation the metallurgical art of processing ores has undergone important changes during the last 25 years. A brief review of the status of each of the following metals is submitted: Cu, Zn, Pb, Cd, Ag, Bi, and Ni. The difficulties of the present electrolytic processes are examined. The importance of precious metal by-products is emphasized. Improvements in process and possible introduction of new methods are discussed. Many novel industrial applications of electrolytic methods to the above and to other metals are suggested.

1201. DUMORTIER, P. (Société générale industrielle chimique, Katanga). [Electrochemistry in the Congo During the War.] *Bull. sci. assoc. ing. élec. Montefiore (Belgium)*, 1946, pp. 231-246; *Chem. Abs.*, vol. 41, 1947, p. 649d.

Electrochemical operations in the Belgian Congo are discussed. They include the production of H₂ and O₂ by electrolysis of water; production of O₂ from air for water purification; Cottrell precipitation of H₂SO₄ mists and Cd fumes; production of ferroalloys; (CaCl₂)-(CaC₂) and sodium silicate in electric furnaces; and electric manufacture of Co, Cu, NaOH, HCl, and NaClO. The last is covered in detail.

1202. ENGELHARDT, VICTOR. *Handbuch der technischen Elektrochemie, Band 1, Tl. 1. Die technische Elektrolyse wässriger Lösungen. Theoret und allgem., Teil A. Die techn. Elektrometallurgie wässriger Lösungen, Eisen, Mangan, und Chrom, Nickel, Kobalt, Zink, Cadmium, Wismut, Antimon, Zinn, Blei, Quecksilber.* [Textbook of Technical Electrochemistry, vol. 1, Part 1. The Technical Electrolysis of Aqueous Solutions. Theoretical and General. Part A. The Technical Electrometallurgy of Aqueous Solutions, Iron, Manganese, Chromium, Nickel, Cobalt,

Zinc, Cadmium, Bismuth, Antimony, Tin, Lead, Mercury.] Ed. by Eger, Georg., Gross, R., Hosenfeld, Martin, and others, Leipzig: Akad. Verlagsges. M. 56; Bound M 58, 613 pp; *Chem. Abs.*, vol. 25, 1931, p. 1166¹.

1203. FORWARD, F. A. Production of Metals by Electrolytic Refining. Blueprint, Vancouver, B. C., November 1946, pp. 20-23; *Eng. Index*, 1947, p. 784.

The advantages of electrolytic processes are enumerated. Presented are power requirements; electrorefining and electrowinning methods for nonferrous metals, Cu, Pb, Ni, Ag, Au, Zn, Cd, and Al.

1204. MACNAUGHTEN, D. J., AND HAMMOND, R. A. F. The Progress of Nickel Deposition in Recent Years. *Metal Ind. (London)*, vol. 34, 1929, pp. 79-82; *Chem. Abs.*, vol. 23, 1929, p. 1353^o.

1205. MANTELL, C. L. Operating Data on Electrolytic Metal Production and Refining. *Eng. and Min. Jour.*, vol. 131, 1931, pp. 256-259; *Chem. Abs.*, vol. 29, 1931, p. 2368.

Operating data from the electrolytic plants of the United States and Canada show: The composition of electrolytes, equipment, methods of applying the current and efficiency obtained from the power, raw materials used, and byproducts produced. The tables cover the electrolytic refining of Cu, the electrolysis of Cu-bearing solutions obtained by leaching processes and the production of Zn, Cd, Pb, Ni, Sn, Ag, and Au. The high cost of processes using insoluble anodes is indicated in the tables. The diaphragm used in Ni production causes an increase in cell voltage with attendant high power costs.

1206. METALLURGIA. Electrolytic Production of Cobalt. Vol. 29, No. 169, November 1943, pp. 37-40; *Eng. Index*, 1943, p. 230.

Reviews recent work on this subject. The electrolysis of cobalt chloride is discussed. Reference is made to an article by C. S. Oldach and R. Landau, indexed from issue of August 1943.

1207. PHILLIPS, W. M. A Century of Progress in Nickel Deposition. *Monthly Rev. Am. Electroplaters Soc.*, vol. 20, No. 2, 1933, pp. 29-34; *Chem. Abs.*, vol. 27, 1933, p. 5649.

A portrayal of the development of Ni plating from 1860 onward; workshop practices, control of solutions, and the deposits, then and now, are contrasted.

1208. TALBOT, H. L., AND CHAPMAN, F. H. How Northern Rhodesia Meets Rising Base Metal Demands. *Eng. and Min. Jour.*, vol. 154, No. 8, August 1953, pp. 82-87; *Eng. Index*, 1953, p. 748.

Features and performance of electrolytic Cu refineries are described. Co, Pb, and Zn are produced, with recovery of V and Cd. Flowsheets are given.

1209. WOHLWILL, H. [Electrolysis in Technical and Economic Competition With Other Methods for Metal Recovery and Refining.] *Metall u. Erz*, vol. 29, 1932, pp. 1-9; *Chem. Abs.*, vol. 26, 1932, p. 2122.

Data are given relative to the scope of electrolytic production and refining of metals. The electrolytic and pyrometallurgical recovery of Cu and Zn are compared, and the broader applications of electrolysis are considered. Other aspects of the problem discussed are the working up of sludge, renewal of bath in refining

impure anodes. As removal and recovery, noble-metal refining, and Pb, Sn, and Ni electrolysis.

1210. ZENTNER, ARTHUR. Electrometallurgical Recovery, Aluminum Leads Metallurgical Field. Eng. and Min. Jour., vol. 139, February 1938, pp. 74-75; Chem. Abs., vol. 32, 1938, p. 2433¹.

An outline of the improvements in the electrometallurgical production of Al, Sb, Co, Cu, Pb, Mg, Ni, Sn, Zn, and Cd is given.

ELECTROWINNING ELECTRORECOVERY OF METALS

1211. BADISCHE ANILIN-UND-SODA-FABRIK (assigned to I. G. Farbenindustrie, A. G. "In Auflösung.") Electrolysis of Nickel-Copper Matte. British Patent 709,000, May 12, 1954; Chem. Abs., vol. 48, 1954, p. 10,463g.

A metallic fraction containing 77 percent of Ni and 19 percent of Cu is separated from the roasted matte by sieving and magnetic separation. The fraction is enclosed in a cotton bag and used as the anode in the electrolytic bath. A very pure Ni salt is formed at the anode while the Cu is recovered as sludge.

1212. BOSQUI, F. L., AND RHOKANA CORP., LTD. [Ferro-cobalt.] French Patent 759,966, Feb. 14, 1934; Chem. Abs., vol. 28, 1934, p. 3314³.

Co is extracted from materials containing Fe and Co, a solution of the metals having been obtained, for example, at the anode. The Fe is removed from the solution, and the Co solution is introduced as catholyte in an electrolytic cell, preferably the same as that in which the anodic solution was made. In this cell, the positive ions of the anode are excluded from the neighborhood of the cathode, and the catholyte is maintained approximately neutral so that precipitation of Co takes place. The anolyte is continually withdrawn and returned after removal of Fe as catholyte. Co is added to compensate for Fe removed. The process is particularly useful for treating material containing Co, Fe, and Cu or other metal lower than Cu in the electrochemical series.

1213. ———. [Ferrocobalt.] French Patent 759,967, Feb. 14, 1934; Chem. Abs., vol. 28, 1934, p. 3314⁴.

A mixture or alloy of Fe, Co, and Cu or other metal lower than Cu in the electrochemical series is corroded electrolytically, and the Fe and Co are deposited together, preferably on a third metal. As claimed in French Patent 759,968, a solution of the mixture or alloy is made, the solution is treated to remove Cu, and then sent to catholyte into an electrolytic cell, in which the anode ions are excluded from the cathode and the acidity is below 3 gm. of H₂SO₄ per l.

1214. FALCONBRIDGE NIKKELVERK, A/S. [Electrolytic Production of Nickel.] Norwegian Patent 56,373, Mar. 30, 1936 (see British Patent 442,622, Feb. 12, 1936, and German Patent 624,652, Jan. 25, 1936 (*Cl. 40c 8*); Chem. Abs., vol. 30, 1936, p. 4768¹); Chem. Abs., vol. 30, 1936, p. 4411².

To produce Ni which can be rolled and annealed and is free from surface irregularities, an electrolyte freed in known manner from such impurities as As, Pb, and Fe is electrolyzed at 25°-45° C. and pH 5.0 to 6.0 with anodes of impure Ni or with insoluble anodes at a current density of 1 a. per cm.² or less. A purified and filtered electrolyte (see Chem. Abs., vol. 27, 1933, p. 1462, and vol. 29, 1935, p. 5755²) is treated with a small quantity of H₂O₂ and electrolyzed at 40° C. with aluminum plates, pH 5.4, and current density 1 a. per cm.²; a Ni electrolyte purified by known methods is treated at 55° C. with KMnO₄, filtered, cooled to 25° C., brought to pH 5.7 with H₂SO₄, and electrolyzed with

a current density of 0.6 a. per cm.²; a Ni electrolyte is oxidized by blowing in air, filtering, adjusting with H₂SO₄ to pH 5.6, cooling to 45° C., and electrolyzing. The Ni obtained contains less than 0.002 percent Fe.

1215. FEDOT'EV, N. P. Pure Cobalt by Electrowinning From Commercial Raw Materials. Jour. Appl. Chem., U. S. S. R., vol. 16, 1943, pp. 241-252 (English summary); Chem. Abs., vol. 38, 1944, p. 5152².

Compact Co was successfully deposited, using Pt anodes; but, as these were uneconomical for commercial use, an attempt was made to substitute other materials. Magnetite, Pb, Pb-Ag, Pb-Sb anodes proved unsatisfactory. Various silicon alloys of Fe, Ni, or Co were tried, and of these the Fe-Si anodes were practical, low in cost, and low in contamination of the solution. However, Fe from the anodes needed to be periodically removed. The raw material for electrolysis was a mixture of cobalt and nickel hydroxides, and was dissolved in 20 to 25 gm. of sulfuric acid per l. in the presence of Na₂SO₄ or SO₂. Directions are given for removal of Fe and Cu by precipitation with sodium carbonate, and for removal of Ni with dimethylglyoxime, which is recovered for reuse. A 99.9-percent Co was produced.

1216. GILL, A. S. Electrolytic Cobalt. Proc. Australasian Inst. Min. and Met., Nos. 152-153, March-June 1949, pp. 73-83; Eng. Index, 1951, p. 225.

In one stage of the purification sequence of zinc sulfate electrolyte used at Risdon, Co is precipitated as cobalt nitroso-beta-naphtholate and is separated from solution by filtration; this precipitate, normally carrying about 1.8 percent Co, is raw material for the production of cobalt oxide, cobalt sulfate, and cobalt metal.

1217. HÄNSEL, GÜNTHER (assigned to Siemens & Halske, A. G.). [Electrolysis of Metals.] German Patent 599,451, July 2, 1934 (*Cl. 40c 1*); Chem. Abs., vol. 28, 1934, p. 5767².

In recovering metals by electrolyzing solutions containing Fe, Ni, Co, or Mn as sulfate, the formation of free H₂SO₄ is avoided by using a partitioned cell and supplying to the anode compartment a solution of Na₂SO₄, capable of combining with H₂SO₄ to form a bisulfate. When Fe is pickled with NaHSO₄ solution, the spent solution may be electrolyzed by the process described, with recovery of NaHSO₄ solution for reuse.

1218. INTERNATIONAL NICKEL CO., INC. [Treatment of Ores, etc., Containing Iron, Nickel, and Copper.] German Patent 620,419, Oct. 21, 1935 (*Cl. 40a 13.50*) (see Canadian Patent 323,286, Chem. Abs., vol. 26, 1932, p. 3998); Chem. Abs., vol. 30, 1936, p. 711².

Describes a process for producing electrolytic Ni, in which the anodes are formed of largely desulfurized Ni-Cu ores, some Ni metal being used to replenish the electrolyte, and some metallic Ni for cementation purification in removing Cu from electrolytes. Gives conditions for electrolysis.

1219. KALLING, B. M. S., SUNDGREN-WALLDEN, R. S. M., WALLDEN, S. J., AND SIVANDER, K. A. (assigned to Bolidens Gruvaktiebolag). Electrolytic Recovery of Nickel. U. S. Patent 2,595,387, May 6, 1952; Chem. Abs., vol. 46, 1952, p. 6530e.

Ni-Cu sponge, obtained from Ni-Cu concentration matte, is leached in a H₂SO₄-H₂SO₃ solution and electrolyzed in a diaphragm cell. The anolyte liquor from the subsequent electrolysis containing 25 gm. of H₂SO₄ per l. with added SO₂ is used to leach the Ni from the sponge and leave the Cu. The leach liquor is then oxidized with air and will be slightly acid, (1.5 gm. of H₂SO₄ per l.) containing 50 gm. of Ni per l. and is fed to the catholyte chamber, which is maintained at 60° C. Current yield will be 70 to 90 percent. If Na₂SO₄ or (NH₄)₂SO₄ is added, the pH of the catholyte may be

raised to 6 without causing precipitation of basic salts and the current yield will be 95 to 100 percent. An insoluble anode and a coarse diaphragm are used. Co-containing metals may be similarly treated.

1220. LAINER, V. I., PLETENEV, S. A., KUZNETZOV, V. A., AND ROZOV, B. I. [Electrodeposition of Nickel With Insoluble Anodes.] *Tsvetnye Metal*, 1931, pp. 1294-1310; *Chem. Abs.*, vol. 26, 1932, p. 5852.

Experiments were made with the object of working out a method for electrodeposition of Ni from Khalila (Russia) ores containing considerable amounts of Fe. Nickel was deposited from NiSO_4 solutions with Al cathodes and Pt anodes. The optimum conditions for the electrolytic treatment of the ore were: Temperature 80°C , concentration of Ni 20 gm. per l., current density 600 a. per m^2 . Acidproof clay diaphragms should be used between the anode and cathode portions of the bath. The anodic and cathodic solutions are circulated separately. The cathodic solution circulates in cascades. As circulating anodic solutions in each bath, Na_2SO_4 solutions of different concentrations are used. The discharged cathode solution contains 1 to 1.5 gm. of Ni and 0.8 to 1.13 gm. of H_2SO_4 per l. The anodic solution contains 6 to 18 gm. of free H_2SO_4 and 25 to 70 gm. of Na_2SO_4 per l. In the continuous process, the anodic solution, after the Na_2SO_4 is crystallized out, may be used for leaching the ores. With rotating cathodes, the deposition of Ni is possible when the Fe : Ni ratio does not exceed 1 : 10. The presence of small amounts of Al (below 0.1 gm. per l.) is desirable.

1221. PALMAER, K. W. [Electrolysis of Metal Solutions With Mercury Cathode.] Swedish Patent 80,333, May 8, 1934 (*see Chem. Abs.*, vol. 28, 1934, p. 422³); *Chem. Abs.*, vol. 29, 1935, p. 3242⁷.

One or more of the metals of the eighth group of the periodic system are deposited from their salt solutions at a Hg cathode. The metal taken up by the Hg is removed continuously or intermittently in a separate vessel or chamber, into which the Hg is conducted from the electrolysis chamber. The Hg is purified by means of liquid containing the purifying substance in solution or in suspension.

1222. PALMAER, K. W., AND GRIEF, O. E. (assigned to Palmaer, K. W.). [Electrolytic Precipitation of Iron, Cobalt, and Nickel.] Swedish Patent 80,334, May 8, 1934; *Chem. Abs.*, vol. 29, 1935, p. 3242⁸.

Details are given of the process of Patent 80,333 (preceding abstract). The purifying substance is applied in a deficient amount so that only part of the total content of metal in the Hg is removed in the purification.

Purifying the Cathode Mercury. Swedish Patent 80,335. A strong oxidizing agent that contains one or more of the metals Fe, Co, and Ni is caused to act upon the Hg.

Method and Apparatus for the Electrolytic Precipitation of Metals. Swedish Patent 80,336. This patent describes the construction of the apparatus, particularly the cathode parts.

1223. RENZONI, L. S. (assigned to International Nickel Co. of Canada, Ltd.). Electrolytic Recovery of Nickel. U. S. Patent 2,480,771, Aug. 30, 1949; *Chem. Abs.*, vol. 43, 1949, p. 8919a.

The constructional details are given for a cell that operates with insoluble anodes and a Cl-containing electrolyte, that does not liberate Cl_2 gas, and that maintains a constant Ni content in the bath. A large number of alternating anodes and cathodes are used, each enclosed by a diaphragm. The anolyte consists of approximately 10 gm. per l. of H_2SO_4 , while the catholyte consists of Ni 40-60, Cl 27-30, and SO_4 71-120 gm. per l. A current density of 20-50 a. per sq. ft. is

used. The anodes are a 6-percent Sb, Pb alloy. Temperatures of 120° - 140°F . are satisfactory.

1224. SHELTON, F. K., STAHL, J. C., AND CHURCHWARD, R. E. Electrowinning of Cobalt From Cobaltite Concentrates. Bureau of Mines Rept. of Investigations 4172, 1948, 98 pp.; *Chem. Abs.*, vol. 42, 1948, p. 2181d.

This report describes the research and pilot-plant studies on the production of Co metal and Co_3O_4 from the cobaltite ores of the Blackbird district, Idaho. A small pilot plant to produce from 4 to 6 pounds of cobalt per day was set up. This pilot-plant operation was considered successful enough to warrant commercial-scale adoption of the process.

1225. SHELTON, F. K., CHURCHWARD, R. E., STAHL, J. C., AND DAVIS, C. W. (Bureau of Mines, Boulder City, Nev.). Electrolytic Cobalt—a Commercially Feasible Process. *Trans. Electrochem. Soc.*, vol. 91, 1947, 17 pp. (preprint) (*see Chem. Abs.*, vol. 40, 1946, p. 3684⁷); *Chem. Abs.*, vol. 41, 1947, p. 1155h.

A method of electrowinning Co from cobaltite ores is described, which has been successfully operated as a pilot plant producing 5 lb. of Co metal per day. The process comprises roasting the ore, extracting the arsenates from the calcine by a caustic leach, extracting the Co from the residual solids in an acid leach, purifying the leach solution, preparing cobalt carbonate from the purified solution, and finally electrodepositing metallic Co from a CoSO_4 electrolyte at 60°C . in a cyclic operation in which the cobalt carbonate is used to neutralize the acid electrolyte. Data, which might prove to be valuable for the estimate and design of a commercial plant, are given, and alternative procedures for different economic and technical conditions are discussed.

1226. SOCIÉTÉ ANONYME "LE NICKEL." Electrodeposition of Nickel. British Patent 288,605, Apr. 13, 1927 (*see French Patent* 643,879, Apr. 13, 1927; *Chem. Abs.*, vol. 23, 1929, p. 1576⁹); *Chem. Abs.*, vol. 23, 1929, p. 568².

Ni is deposited from a nickel chloride solution in a diaphragm cell with anodes of impure Ni. The spent catholyte is passed to the anode chamber. The liquid from the anode chamber is treated with $\text{Ni}(\text{OH})_2$ in a separate vessel to precipitate Fe, Co, As, and other impurities and returned to the cathode chamber at a temperature above normal. The electrolyte is maintained at a density of 1.2 to 1.3 corresponding to 150 kg. of Ni per m^3 . Nickelous hydroxide and air may be used in place of $\text{Ni}(\text{OH})_2$. Crude alloys before formation into anodes are refined by converting the greater part of the Fe into slag to obtain a Ni content of 90 to 95 percent. Anodes may be produced from the oxidized ores of New Caledonia. Various details and modifications are described.

1227. SOCIÉTÉ GÉNÉRALE DE CONSTRUCTIONS ÉLECTRIQUES ET MÉCANIQUES (assigned to Als-Thom.). [Cobalt.] French Patent 750,097, Aug. 3, 1933; *Chem. Abs.*, vol. 28, 1934, p. 420⁸.

Pure Co is obtained as a powder by electrolyzing a solution of a cobalt salt, preferably pure sulfate, the density of the current is 500 to 5,000 amperes per dm^2 , according to the size of grain desired, and the temperature, is 40° - 60°C . Means are provided to remove the Co periodically from the cathode.

1228. TALBOT, H. L., AND HEPKER, H. N. Investigations on Production of Electrolytic Cobalt From Copper-Cobalt Flotation Concentrate. *Inst. Min. and Met. Bulls.* 518 and 522, January 1950, pp. 31-35 (author's reply, May 1950, pp. 37-40); *Eng. Index*, 1950, p. 228.

A discussion of paper in *Engineering Index*, 1949, p. 219, from *Bulletins* 514 and 517, September and December 1949, is presented.

1229. THEYS, L. (Union minière du Haut Katanga, Jadotsville, Belgian Congo). [Metallurgy of Cobalt at the Union Minière du Haut Katanga.] Commem. Cinquantième anniv. Comité spec. Katanga, Compt. rend. congr. sci. Elisabethville, vol. 3, 1950, pp. 169-187; Chem. Abs., vol. 46, 1952, p. 7951d.

Historical review of process used during the past 40 years. Co is present in the ores mainly as the higher oxides; these are dissolved by adding FeSO_4 to the leach liquors. Co is recovered from the electrolytic solutions after deposition of Cu, by fractional precipitation of hydrated Co oxides at pH 7 and electrolysis at pH 6.5 of cobalt sulfate solutions containing excess of hydrated oxides to react with the acid formed during the electrolysis.

1230. TURNER, J. L., AND ALESSANDRONI, H. B. (assigned to National Lead Co.). Electro Recovery of Metals. U. S. Patent 2,529,237, Nov. 7, 1950; Chem. Abs., vol. 45, 1951, p. 1440f.

A method of electrorecovery is described which is particularly applicable to Fe and Mn and suitable also for other metals, such as Ni, Co, Cu, Zn, Cd, Sn, and Pb. The cathode consists of a conducting screen (12- to 24-mesh) of the same or other metal than the one being deposited. Heavy and dense deposits that do not peel are obtained. These screen anodes, in place of the sheet-metal cathodes heretofore employed, permit free circulation of electrolyte between the two sides of the cathode, providing for better adherence, and no losses to treeing. Slabs up to 0.3 inch of iron have been made.

1231. WESLEY, W. A. (International Nickel Co., Bayonne, N. J.). The Electrochemistry of Nickel. Ind. Eng. Chem., vol. 44, 1952, pp. 957-965; Chem. Abs., vol. 46, 1952, p. 6527e; Metals Review, vol. 25, No. 7, July 1952, p. 27 (88c).

The present knowledge of the electrochemical reactions of Ni as applied to industry is reviewed. Most industrial electrolytes for the electrodeposition of Ni are based on a $\text{NiSO}_4\text{-NiCl}_2\text{-H}_3\text{BO}_3$ solution, which is modified to produce Ni deposits of different mechanical properties, metallographic structure, or surface brightness. It is possible to electrodeposit sound Ni metal at speeds much higher than have yet been used commercially. Industrial processes discussed include electrorefining, electroforming, electroplating, resizing of mismachined or rejected parts, and electropolishing.

1232. WILLIAMS, A. I. W. The Production of Nickel Sheets by Electrodeposition. Metal Ind. (London), vol. 49, 1936, pp. 215-219; Chem. Abs., vol. 30, 1936, p. 7459^o.

1233. ZHURIN, A. I., AND KAVITSKAYA, S. [Production of Nickel by Electrolytic Refining of Alpha Garnierite Matte.] Tsvetnye Metal, vol. 15, No. 1, 1940, pp. 80-85; Chem. Zentralb., vol. I, 1941, p. 1221; Chem. Abs., vol. 36, 1942, p. 6417^o.

Experiments were made on electrolytic refining of a garnierite matte of composition Ni 76.4, Cu 4.6, Fe 0.07, and S 18.78 percent. The time required was 2 days or less, at 75 a. per m.² and 80° C. The energy consumed was 1.95 kw.-hr. per kg., for example, approximately as much as in refining black nickel oxide. The extraction was 95 percent for nickel at a 90-percent current efficiency. The anode efficiency was lower, 20 to 30 percent of the current being spent on oxidation of S at the anode. The electrolyte became enriched in SO_4 and impoverished in Ni; consequently, NiO had to be added periodically. The anode slime amounted to 25 percent of the loss of weight of the anode (0.2 to 0.4 gm. per a.-hr.). It contained 15 to 25 percent Ni and adhered firmly to the anode, but without interfering with the progress of the electrolysis if the latter was of short duration.

1234. ZHURIN, A. I., AND ZVEREVICH, N. V. [Anodic Solution of Cobalt-Nickel Ores.] Trans. Leningrad Ind. Inst. Sec. Met., No. 4, 1940, pp. 98-104 (German summary); Chem. Abs., vol. 40, 1946, p. 2744^o.

Co-enriched slags from roasted crude Cu-Ni (Fe-Co) sulfide ores were mounted as an anode enclosed in a canvas bag between two Cu cathodes in H_2SO_4 solution. The current efficiencies of anode and cathode and the degree of metal extraction were studied at temperatures of 40°-60° C. and current densities of 100 to 250 a. per m.². The percentage of total current expended at the anode was 60 to 80 percent and at the cathode 5 to 10 percent, with a metal extraction of about 70 to 90 percent with 194 ampere-hr. With higher temperature and current density, the anodic current efficiency and percentage extraction increase at the expense of energy consumption. A slime is formed, which, after removal of S, can be reused as anode.

ELECTRODEPOSITION OF METALS

1235. BOLIDENS GRUVAKTIEBOLAG. Recovering Metals of the Iron Group. British Patent 636,874, May 10, 1950; Chem. Abs., vol. 44, 1950, p. 7680d.

Fe, Ni, and Co are recovered by electrolysis in a diaphragm cell. The catholyte is a slightly acid sulfate of the metals recovered.

1236. BOSQUI, F. L. (assigned to Rhokana Corp., Ltd.). Electrodeposition of Cobalt. U. S. Patent 2,045,212, June 23, 1936 (see British Patent 416,528; Chem. Abs., vol. 29, 1935, p. 1021^{5,6}); Chem. Abs., vol. 30, 1936, p. 5509^o.

1237. — (assigned to Rhokana Corp., Ltd.). Ferrocobalt. U. S. Patent 2,051,433, Aug. 18, 1936; Chem. Abs., vol. 30, 1936, p. 6658^o.

An alloy containing Fe, Co, and substantially more than 15 percent of Cu is anodically corroded in an electrolytic cell, the electrolyte of which contains acid in an amount less than 3 gm. per l., calculated as H_2SO_4 ; this produces in the cell a cathode deposit of Co and Fe containing less Cu than the anode, and the treatment is repeated if necessary until the product contains 15 percent or less of Cu. The material is then anodically corroded in a cell, where the electrolyte acidity is less than 3 gm. per l. calculated as H_2SO_4 , and with a Cu content not exceeding about 0.05 gm. per l., so that Fe and Co substantially free from Cu are deposited, the greater part of the Cu remaining in the cell as sludge. An apparatus arrangement is described.

1238. BOZEL, MALETRA (assigned to Société Industrielle de produits chimiques). [Electrolytic Depositions.] French Patent 807,530, Jan. 14, 1937; Chem. Abs., vol. 31, 1937, p. 5280^o.

A suitable bath contains salts of Ni and Co, boric or acetic acid or their salts, and one or more salts containing chlorides, fluorides, bromides, or sulfates of metals especially of alkalis; the bath is used at a temperature of 5°-90° C., pH 2.5 to 4.5, current density of 0.5 to 20 a. per dm.²

1239. BROWN, HENRY (assigned to Udyllite Corp.). Electrodeposition of Nickel. U. S. Patent 2,694,041, Nov. 9, 1954; Chem. Abs., vol. 49, 1955, p. 3697d.

The grain size and luster of electrodeposited Ni can be increased by plating from baths containing $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ 250-300, $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ 35-75, H_3BO_3 35-40, and coumarin sulfonic acid 0.5-3.0 gm. per l. Plating can take place at 40°-65° C., pH of 2.5-4.5, and a current density range of 5-150 a. per ft.²

1240. CHIZHIKOV, D. M., AND USTINSKII, B. Z. [Electrolysis of Nickel Sulfate in a Cell With Nonfiltering Diaphragm.] Zhur. Priklady Khim., vol. 22, 1949, pp. 1306-1309; Chem. Abs., vol. 49, 1955, p. 9406b.

Electrolysis of NiSO_4 was carried out at 45-50°

C. in a cell consisting of 2 concentric, ceramic, unglazed cups with a Ni cathode and a Pb anode in the central and outside cups. The anolyte contained Na_2SO_4 and 10 to 60 gm. per l. H_2SO_4 ; the catholyte NiSO_4 , H_2BO_3 , KCl, and variable concentrations of H_2SO_4 . With 40 to 60 gm. per l. of H_2SO_4 in the anolyte, diffusion was sufficient to maintain acidity in the catholyte constant; otherwise, it was made up by the circulation of a neutral or slightly acid solution of $\text{NiSO}_4 + \text{H}_2\text{BO}_3$. Dense deposits of Ni were obtained from solutions of 3 gm. per l. of H_2SO_4 with a current density of 250 a. per m^2 and a current efficiency of 60-70 percent. The last was somewhat higher with 500-1,000 than with 250 a. per m^2 from a solution containing 12-15 gm. per l. of H_2SO_4 .

1241. CUPEY, M. E. (assigned to E. I. du Pont de Nemours & Co.). Electrodeposition of Nickel, Copper, or Lead. U. S. Patent 2,318,592, May 11, 1943; Chem. Abs., vol. 37, 1943, p. 5913².

Deposition of these metals as for electroplating is effected from an aqueous solution containing the metal as cation and the sulfamate ion, which serves for use in either an acid or alkaline plating bath.

1242. FALCONBRIDGE NIKKELVERK AKTIESELSKAP. [Electrodeposition of Nickel.] German Patent 606,105, Nov. 24, 1934 (*Cl. 40c 8*) (see French Patent 760,810, Chem. Abs., vol. 28, 1934, p. 3989³); Chem. Abs., vol. 29, 1935, p. 1331⁷.

In deposition of Ni electrolytically, the plates to become the cathodes are first subjected to the action of acid, such that, while the plate is cleaned, it is not attacked; the plates are then introduced into the electrolytic bath without further treatment and while still damp.

1243. ———. [Nickel.] French Patent 772,696, Nov. 3, 1934 (see British Patent 420,248, Nov. 28, 1934; Chem. Abs., vol. 29, 1935, p. 3242⁹); Chem. Abs., vol. 29, 1935, p. 1332⁵.

A solution of Ni salts containing some Fe and also impurities considered too considerable up to the present, is first electrolyzed under such conditions as to deposit the impurities along with some Ni; the purified electrolyte is now used in the ordinary manner for electrolysis.

1244. ———. Reducing Oxides of Nickel, etc. British Patent 423,951, Feb. 12, 1935 (see German Patent 598,334, Chem. Abs., vol. 28, 1934, p. 5392⁸); Chem. Abs., vol. 29, 1936, p. 5062².

1245. FEDOT'EV, N. Extraction of Pure Cobalt by Electrolysis. Trans. Electrochem. Soc., vol. 87, 1945, 3 pp. (preprint); Chem. Abs., vol. 39, 1945, p. 872⁶.

Starting with a crude cobalt oxide cake, this is converted into CoSO_4 , and electrolyzed in a diaphragm cell, with duriron anodes. Catholyte and anolyte are separately circulated and regenerated. Excess Fe in the anolyte is removed by Na_2CO_3 , and the Ni in the catholyte by dimethylglyoxime; this keeps these impurities very low in concentration. The cathode deposit analyzed Co 99.9, Fe 0.02, and Ni 0.05 percent.

1246. GEORG REUTER GALVANOTECHNISCHE FABRIK. [Nickel.] German Patent 638,551, Nov. 17, 1936 (*Cl. 48a 6.05*); Chem. Abs., vol. 31, 1937, p. 2944¹.

In the electrolytic separation of Ni, soluble anodes of Al, Mg, or light metals are used.

1247. GRONNINGSÆTER, A. M. (assigned to Falconbridge Nickel Mines, Ltd.). Malleable and Annealable Nickel. Canadian Patent 405,917, July 7, 1942; Chem. Abs., vol. 36, 1942, p. 5432⁷.

On a cathode suspended in a porous bag of the Hybinette type, Ni is deposited from an electrolyte containing traces of impurities, at pH 1.5 to 3.5, a temperature of 50°-70° C., and a current density of 0.5 to

5.0 a./dm.² Minute air bubbles released at the bottom and within the cathode bag rise outside the cathode, stirring the Ni electrolyte with surrounding electrolyte to prevent an accumulation of pit-forming gas bubbles and adherence of pit- and berry-forming solid impurities on the cathode.

1248. ——— (assigned to Falconbridge Nickel Mines, Ltd.). [Electrolytic Recovery of Nickel.] German Patent 812,611, Sept. 3, 1951 (*Cl. 40c 8*); Chem. Abs., vol. 47, 1953, p. 4228e (see British Patent 667,659); Chem. Abs., vol. 46, 1952, p. 6974c.

1249. HALL, NATHANIEL, AND HOGABOOM, G. B., JR. Nickel Salts From Nickel Anodes, Porous-Pot Method. Metal Finishing, vol. 49, 1951, pp. 66-69, 70; Chem. Abs., vol. 45, 1951, p. 6090b.

Scrap Ni anodes were mounted in porous pots as anode with 10 percent H_2SO_4 or 20 percent HCl. In 6 hours, an appreciable deposition of Ni on the cathode had occurred; the current employed had dropped to a quarter of its original intensity and the acid to 0.1 percent. The sludge was now dissolved, producing a solution from which Ni salts could be obtained.

1250. HARSHAW CHEMICAL CO. [Depositing Metals.] French Patent 781,552, May 18, 1935; Chem. Abs., vol. 29, 1935, p. 6156².

The electrolysis of a solution of a compound of the metal to be deposited takes place in the presence of a small amount of the reaction product of a terpenoid with H_2SO_4 . The terpenoid may be a resin, resin oil, neutralized resin oil, turpentine oil, pine oil, or cedarwood oil.

1251. HIRUMA, KOICHI. [Electrolytic Manufacture of Nickel Powder.] Jour. Electrochem. Soc., Japan, vol. 17, 1949, pp. 160-161; Chem. Abs., vol. 44, 1950, p. 5228h.

The mechanism of the formation of Ni powder was discussed in relation to that of Cu and Fe powders. The voltage-current curve, the effects of the concentration of the Ni salt, additional electrolytes, and pH values are considered. The optimum conditions for the formation of fine Ni powder are: Concentration of ammonium sulfate in electrolyte 0.2 to 2.0 normal; pH 2.0 to 4.0; about 10 volts.

1252. KALLING, B. M. S., SUNDGREN-WALLDEN, R. S. M., WALLDEN, S. J. AND SIVANDER, K. A. (assigned to Bolidens Gruvaktiebolag). [Recovery of the Metals of the Iron Group by Electrolysis in a Cell Provided With a Diaphragm and Insoluble Anodes.] Swedish Patent 138,011, Nov. 11, 1952; Chem. Abs., vol. 47, 1953, p. 5282a.

Using an electrolytic cell with diaphragm (suitably of nitrated cellulose or glass or mineral fibers) and equipped with insoluble anodes, a feed material of Fe, Ni, or Co in sponge-metal form dissolved in acid and nearly neutralized, the solution is led into the catholyte chamber where the pH is kept just below neutral for efficient deposition; a device circulates the catholyte back to the anolyte chamber, resulting in a strongly acid anolyte to dissolve fresh material and a weakly acid catholyte.

1253. LATER, E. P. The Electrodeposition of Cobalt. The Foundry, March 1916, pp. 111-113; Bureau of Mines Inf. Circ. 6331, p. 31.

Presents results of experiments carried out by Kalmus, Harper, and Savell working under the direction of the Canadian Bureau of Mines.

1254. MOND NICKEL CO., LTD. Electrodeposition of Nickel. British Patent 615,036, Aug. 16, 1946; Canadian Patent, Sept. 6, 1945; British Abs., 1950, p. B-I-127.

Thick, ductile, adherent, nonstreaky deposits are produced on Zn or Zn alloys by plating at a current

density of 15 to 90 a. per ft.² from a bath containing $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 15–100 (preferably 20–40) and tartaric acid 20–150 (preferably 30–60) gm. per l. and adjusted to pH 5 to 7.2 (preferably 5.3–6.2) with aqueous NH_3 .

1255. ———. Electrodeposition of Nickel on Nickel. British Patent 617,689, Oct. 16, 1946; Canadian Patent, Oct. 25, 1945; British Abs., 1950, p. B-1-127.

Bonding of electrolytically deposited Ni to a Ni cathode is achieved by anodically treating the cathode at a current density of 10 to 25 a. per ft.² for not less than 5 minutes in a bath containing H_2SO_4 (90–200) and Cu^{++} 0.5–30 (preferably 2–10) gm. per l.

1256. ———. Electrodeposition of Nickel on Nickel. British Patent 618,322, Oct. 16, 1946; Canadian Patents, Oct. 25, 1946, and Dec. 3, 1945; British Abs., 1950, p. B-1-127.

Bonding of electrodeposited Ni to a Ni cathode is improved by first dipping or anodically treating the cathode in a solution containing Cl^- (NaCl) not more than 9, Cu^{++} 0.5–30 (preferably 2 to 10) gm. per l. HCl (50–200 gm. per l.) may be included both to render the bath acid and to supply Cl^- .

1257. ———. Electrorefining and Electroplating. British Patent 622,015, Apr. 26, 1949; Chem. Abs., vol. 43, 1949, p. 6527b.

In a Ni plating bath, conditions can be adjusted so as to corrode the whole anode, rather than corrode the weld preferentially. The chloride concentration should be from 0.4–2.8 normal, the pH from 2–4.

1258. ———. Electrodeposition of Nickel. British Patent 659,335, Apr. 14, 1949; U. S. Patent, Apr. 22, 1948; British Abs., 1952, p. B-I-396.

The electrolyte contains $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 100–400 (preferably 250–350), and H_3BO_3 10–50 (preferably 20–40) gm. per l. is free from Cl , has a pH of 0.75–3.5 (preferably 1–2), and is at a temperature of 38°–71° C. An insoluble anode is used, and the Ni content of the electrolyte is replenished by passing direct current through it between Ni electrodes so that the anode efficiency is higher than the cathode efficiency, the current density being 1–25 (preferably 5–15) a. per ft.² and the direct current being reversed at intervals of 1–50 (3–7) seconds.

1259. MOROCHOV, M. I., STEPANOV, D. V., AND MOROKO, S. [Electrodeposition of Nickel in the Presence of Arsenic.] Jour. Appl. Chem., Russia, vol. 13, 1940, pp. 1322–1325; British Abs., 1945, p. B-I-37.

Ni was deposited on stainless steel from a bath consisting of NiSO_4 140, NiCl_2 10, H_3BO_3 10 gm. per l. and some NaAsO_2 ; then the Ni films were stripped off. The H₂ content of the Ni films had a maximum (about 4 volumes of H₂ per volume of Ni) at an As_2O_3 content of 50 mg per l. At the same As_2O_3 content, the CO content had a maximum of 1.4 volumes. The As content of the films increased regularly with the As_2O_3 content of the solution (25–200 mg. per l.), and the tensile strength decreased from 99 kg. per mm.² for pure Ni to nil at 1.41 percent of As. The Ni bath should contain less than 10 mg. As_2O_3 per liter.

1260. NISHIHARA, KIYOKADO. [The Recovery of Cobalt From Its Sulfate Solution by the Electrolytic Process.] Suiyokwai Shi, vol. 9, 1938, pp. 355–364; Chem. Abs., vol. 32, 1938, p. 3270¹.

Various temperatures, electric current densities, pH values, and salt concentrations were tried in an effort to deposit Co from CoSO_4 solution. If the pH rose too high a blue-black deposit was formed, a hydrated oxide. Using normal H_2SO_4 saturated with SO_2 or a NaSO_3 or tetrathionate solution, and a sufficiently strong cobalt sulfate, good compact deposits were obtained at above 50° C.

1261. OKADA, SHINZO. [Electrolytic Casting of Metals.] Japanese Patent 329 ('50), Feb. 8, 1950; Chem. Abs., vol. 46, 1952, p. 7444b.

The electrolyte to be used for the electrodeposition of metals on the metal product is $\text{Cu}(\text{BF}_4)_2$ for Cu, $\text{Ni}(\text{BF}_4)_2$ for Ni, and $\text{Fe}(\text{BF}_4)_2$ for Fe; the electrodeposition is made in the presence of excess BF_3 and H_3BO_3 at a current density of more than 10 a. per dm.²

1262. PILLING, N. B., AND WESLEY, ANDREW. Nickel Flakes. U. S. Patent 2,365,356, Dec. 19, 1944; Chem. Abs., vol. 39, 1945, p. 4289².

Extremely thin Ni flakes are produced electrolytically. Soluble or insoluble anodes are used, a bath temperature of about 15° C., and current density 25 a. per ft.². Suitable cathodes are made of Al, Ta, Inconel, or stainless steel, to which the deposited Ni adheres very feebly. A leaching agent, such as stearic acid, about 1 percent, and a promoter, such as aluminum stearate, about 1 percent, are used. For insoluble anodes, a bath of nickel-ammonium sulfate 100, and ammonium hydroxide 137 gm. per l. is used; for soluble anodes nickelous chloride 60, ammonium hydroxide 14, and ammonium hydroxide 137 gm. per l. is recommended. The powder is useful in paints and Ni painted paper.

1263. PINE, P. R. Electrodeposition of Metals Such as Nickel. U. S. Patent 2,029,386-7, Feb. 4, 1936; British Patent 436,042, Oct. 3, 1935 (see French Patent 781,552, Chem. Abs., vol. 29, 1935, p. 6156²); Chem. Abs., vol. 30, 1936, p. 1669⁴.

1264. PIONTELLI, ROBERTO, AND GIULOTTO, ALESSANDRO. [Electrodeposition of Metals From Solutions With Sulfamic Acids or Its Salts.] *Chimica e industria* (Italy), vol. 21, 1939, pp. 478–491 (see L. Cambi and R. Piontelli, *Rend. inst. lombardo sci.*, vol. 72, 1938–1939); Chem. Abs., vol. 34, 1940, p. 677¹.

Conditions for electrolytically depositing metals from solutions or salts of sulfamic acid were investigated; of these metals Ni and Co can either be deposited as a protective coating or refined electrolytically; other metals investigated for deposition were Cu, Fe, Cd, Rh, Ag, Pb, and Zn, which proved successful; unsuccessful were Sn, Mn, Bi, Cr, Sb, and As.

1265. RYMERSHOLMS GAMLA IND. AKTIEBOLAG. Electrolytic Production of Metals (Cobalt, Nickel, Iron). British Patent 625,585, Dec. 17, 1946; British Abs., 1950, p. B-I-294.

A bath containing 12 to 16 gm. of Co, Ni, or Fe (as formate) per l. is electrolyzed at 150–350 (350) a. per m.²; spent electrolyte is continuously withdrawn, used to dissolve more metal, and returned to the cell.

1266. SMITH, S. C. Electrodeposition of Nickel. British Patent 314,579, Mar. 30, 1928; Chem. Abs., vol. 24, 1930, p. 1301⁹.

In the deposition of Ni from a nickel sulfate solution, using insoluble anodes, the electrolyte is maintained at low acidity by conversion of the free acid formed, as electrolysis proceeds, into $(\text{NH}_4)_2\text{SO}_4$, as by continuous or intermittent addition of NH_3 . A pH of 3.5–6.5 is suitable and cathodes of Al or Al alloys are used. Electrolysis is stopped when the Ni content of the electrolyte falls to 0.05 percent; the residual liquor is concentrated and cooled for removal of nickel-ammonium sulfate by crystallization and further concentrated for recovery of $(\text{NH}_4)_2\text{SO}_4$; or the residual Ni may be precipitated by adding $(\text{NH}_4)_2\text{S}$ followed by crystallization of $(\text{NH}_4)_2\text{SO}_4$. Various other details for regulating the process are given.

1267. SOCIÉTÉ D'ÉLECTROCHIMIE, D'ÉLECTROMÉTALLURGIE ET DES ACIÈRES ÉLECTRIQUES D'UGINE. [Nickel Sulfate.] French Patent 983,071, June 6, 1951; Chem. Abs., vol. 49, 1955, p. 2225f.

Nickelous sulfate is prepared by electrolysis of H_2SO_4 with a Ni anode and an insoluble cathode. For example, 2N H_2SO_4 is electrolyzed in a Pb vessel containing a Pb or Ni-Cu cathode and an anode of scrap Ni at a cathode current density of 22 a. per dm.², an anode current density of 4.5 a. per dm.², and a potential difference of 5 volts. When the electrolysis is complete (at a density of 37° B.), the solution is concentrated to crystallize it. The mother liquor is recycled.

1268. TENNANT, W. J. Electrodeposition of Nickel. British Patent 513,963, Apr. 23, 1938; British Chem. Abs., 1940, p. B-55.

A bath for direct plating of Ni on steel contains $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ 32, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 6, and H_3BO_3 4 oz. per gal., to which is added a substance to maintain the grain size of the plate below that at which pitting occurs, for example, PhOH 2.5, naphthaquinone 1, phenolphthalein 15, and a sulfide, chloride, cyanide, carbonate, hydroxide, or oxide of Cd, Zn, Sn, Co, or Pb 2 oz. per gal.

1269. UNION MINIERE DU HAUT KATANGA, AND REDDIE, L. N. Treatment of Solid Materials in Electrolytes. British Patent 577,568, May 23, 1946; Chem. Abs., vol. 42, 1948, p. 6251e.

Nonferrous metals (for example, Co or Ni) are recovered from materials containing an oxide of the metal by electrolyzing an acid solution containing the metal in solution and the materials in suspension in finely divided form. The pH of the acid solution is kept between 4.5 and 6 by regulating the rate of delivery of the finely divided solids to the solution. Preferably, the finely divided solids are added to the solution being electrolyzed at a rate proportional to the rate of deposition of the metal on one of the electrodes. The electrolysis is conducted in an electrolytic cell having a cathode and an insoluble anode but having no diaphragm.

1270. WEISBERG, LOUIS, AND STODDARD, W. B., JR. Electrodeposition of Ni, Co, and Ni-Co Alloys. British Patent 464,814, Apr. 26, 1937 (*see* Chem. Abs., vol. 30, 1936, p. 1312³); Chem. Abs., vol. 31, 1937, p. 6565⁷.

The metals are deposited from a bath of their sulfates and/or chlorides containing an ammonium salt and formaldehyde or formates at a pH of 4 to 4.5. A suitable bath for deposition of the alloy contains NiSO_4 240, NiCl_2 45, CoSO_4 15, nickel formate 45, $(\text{NH}_4)_2\text{SO}_4$ 1, and HCHO 0.5–1.0 gm. per l.

1271. ZVYAGINTSEV, O. E., AND PLAKSINA, L. D. [Rational Phase Analysis of Slimes From Nickel Analysis.] *Izvest. Sektora Platiny i Drugikh Blagorodnykh Metal.* Inst. Obshchei i Neorg. Khim., Akad. Nauk, S. S. S. R., No. 22, 1948, pp. 95–110; Chem. Abs., vol. 44, 1950, p. 10, 548e.

The object of this investigation was to determine in what state Ni was present in electrolytic slimes, that is, as metal, sulfate, sulfide, or oxide.

The dried and ground slime contained 30.54 percent of Ni with small amounts of Cu, Fe, silica, Ca, S, sulfates, etc. The sulfate was dissolved in water; the residue was boiled with 2 percent copper sulfate for 4 hr., removing all metallic Ni, and 17 percent of the sulfide Ni; the residue was boiled twice for 1 hour with a mixture of acetic acid, H_2O_2 , and H_2O to remove the rest of the sulfide Ni; the last residue was treated with aqua regia to dissolve oxides of Ni.

ANODES FOR ELECTROLYSIS

1272. ALKAN, M. L. Soluble Electrolytic Anodes. British Patent 572,168, June 30, 1943; British Abs., 1946, p. B-1-8.

Metal anodes are made with corrugated oval cross section to withstand crumbling and to have superior throwing power.

1273. BARATTINI, A. [Nickel Anodes.] *Ind. meccan.* (Milan), vol. 17, 1935, pp. 9–12; Chem. Abs., vol. 29, 1935, p. 3239⁹.

The points of view that should determine the selection of Ni anodes are discussed. Cast anodes, even if pure enough, have a low efficiency because they disintegrate irregularly and leave undissolved much non-recoverable scrap. Bright, rolled anodes become passive. Annealed rolled electrodes with mechanically roughened surface go into solution uniformly and give a much higher efficiency than the two types mentioned, and are suitable for concentrated baths with medium current density. Anodes cut from Ni-refinery cathodes are serviceable providing the Cl^- content of the bath is regulated. Cl^- addition is recommended for medium or high current densities.

1274. BECKER, ERICH. [Nickel Anodes.] *Metallbörse*, vol. 22, 1932, pp. 1293–1294 and 1325–1326; Chem. Abs., vol. 28, 1934, p. 47⁵.

A review is given.

1275. BIEBER, C. G., AND BUCK, M. P. (assigned to International Nickel Co.). Nickel Anodes for Use in Electroplating. U. S. Patent 2,117,284, May 17, 1938 (*see* Canadian Patent 376,237, Sept. 6, 1938, Chem. Abs., vol. 32, 1938, p. 8284⁷); Chem. Abs., vol. 32, 1938, p. 4888⁴.

Anodes are formed of Ni together with C about 1 percent, Mg and Ti about 0.25 to 0.28 percent each, Si about 0.55 percent, Co about 0.35 percent, Fe about 0.14 percent, Cu about 0.1 percent, and Mn about 0.12 percent. Such anodes can be rolled substantially free from cracks.

1276. BIEBER, C. G., AND TSCHOP, H. E. Nickel Anodes. U. S. Patent 2,304,059, Aug. 12, 1942; British Abs., 1944, p. B-1-246.

An electroplating anode having increased activity, more uniform corrosion, greater sludge adherence, and less tendency to produce loose Ni than conventional C-containing anodes contains C 0.2–0.3, S 0.007–0.1 Si 0.2–0.25, Mg 0.05–0.07, Cu not more than 0.1, Mn not more than 0.01, and Fe not more than 0.1 percent.

1277. BULAKH, A. A., AND KHAN, O. A. Structure of Nickel-Copper Anodes in the Process of Slime Formation. *Jour. Appl. Chem.*, U. S. S. R., vol. 27, 1954, pp. 97–98 (English trans.) (*see* Chem. Abs., vol. 48, 1954, p. 6878g); Chem. Abs., vol. 49, 1955, p. 5160d.

1278. CHIZHIKOV, D. M., AND USTINSKII, B. Z. (A. A. Baikov Metallurgical Institute Academy of Sciences, U. S. S. R., Moscow). [Electrochemical Solution of Metal Sulfides.] *Izvest. Akad. Nauk, S. S. S. R., Otdel Tekh. Nauk.*, 1948, pp. 229–234; Chem. Abs., vol. 42, 1948, p. 6675i.

Artificial sulfide anodes weighing 300–350 gm. were prepared and subjected to anodic dissolution over a period of time of approximately 12 hr. in H_2SO_4 . In general, the current rises during this time, current efficiency varies in the range 60–70 percent. The current density, voltage, current efficiency, and chemical composition of the solutions, and sludges are detailed for sulfides of Cu, Ni, and Co.

1279. DEUTSCH & BRENNER, LTD., AND TAYLOR, E. L. Nickel Anodes for Electroplating or Electrodepositing. British Patents 520,211 and 520,212, Nov. 22, 1938; British Chem. Abs., 1940, p. B-620.

(A). The anode comprises strips of electrodeposited Ni welded together to give electrical connection, thus forming a multiplex anode structure.

(B). An anode giving increased throwing power comprises three electrically connected plates, the middle

1 being wider than the other 2, to give a cruciform shape.

1280. FALCONBRIDGE NIKKELVERK AKTIESELSKAP. Annealing Nickel Plates for Use as Anodes. British Patent 423,370, Jan. 31, 1935 (this corresponds to French Patent 760,809, Chem. Abs., vol. 28, 1934, p. 3990^a); Chem. Abs., vol. 29, 1935, p. 4320^a.

The melt may also contain a scavenging substance (for example, borax or other boron compound) in quantity up to 25 percent.

1281. GEIGER, G. F. (assigned to International Nickel Co., Inc.). Uniform-Corrosion Anode. Canadian Patent 333,247, June 13, 1933; Chem. Abs., vol. 27, 1933, p. 4525.

To a melt of commercial Ni is added 0.002–0.020 percent S. Oxygen (0.02–0.25 percent) is introduced by flapping and the melt is poured. The ingots formed are forged, rolled to anode shape, and cooled in water containing 20 percent of alcohol.

1282. — (assigned to International Nickel Co.). Nickel Anodes. U. S. Patent 1,941,256, Dec. 26, 1934; Chem. Abs., vol. 28, 1934, p. 1282^a.

Rolled or cast Ni anodes containing S 0.002–0.0075 percent and containing O₂ corrode with smooth surfaces and substantially to anode sludges. United States Patent 1,941,257 relates to a similar addition of S in small proportion to Ni-bearing material before pouring.

1283. — (assigned to International Nickel Co.). Extruded Nickel Plating Anodes. U. S. Patent 2,274,056, Feb. 24, 1942; Chem. Abs., vol. 36, 1942, p. 3738^a.

The metal is extruded under pressure at 900° C.–1200° C. to form an anode with nonuniform grain size. This anode corrodes smoothly, as do rolled electrodes, and produces no more loose Ni or sludge.

1284. GRONNINGSÆTER, A. M. (assigned to Falconbridge Nickel Mines, Ltd.). Nickel Cathodes for Subsequent Use as Anodes in Plating. U. S. Patent 2,143,913, Jan. 17, 1939; Chem. Abs., vol. 33, 1939, p. 2824^a.

The anodes are made more readily soluble for a subsequent operation by immersing them in a bath of molten salts at an elevated temperature. They are protected by a salt coating while being quenched after the immersion.

1285. HULL, R. O. (assigned to E. I. du Pont de Nemours & Co.). Nickel Anode Production. U. S. Patent 2,297,766, Oct. 2, 1942; British Abs., 1944, p. B-I-34.

Electrolytic Ni cathodes, or castings made by remelting electrolytic Ni, are rendered suitable for use as anodes by heating at 500°–1,000° C. (800° C.) to allow crystal transformation to take place, and then quenching in not less than 73 percent (preferably 92–100 percent) H₂SO₄.

1286. INTERNATIONAL NICKEL CO., INC. Production of Massive Nickel for Use as Anodes. British Patent 553,781, Sept. 2, 1942 (addition to British Patent 539,882, 1942, p. B-I-66); British Abs., 1943, p. B-I-382.

Nickel containing 0.01–0.25 percent of S is deposited electrolytically (at 25°–50° C., current density 10–50 a. per ft.², pH 1.7–6.0) from a bath containing a water-soluble Ni salt, a Ni salt, a buffer, and one or more S compounds, such as a sulfonamide (0.2–1.0 gm. per l.), a thiourea (0.02–0.12), a phenothiazine (0.05–0.20), a thiosulfate (0.05–0.20), and a dithiophosphate (0.10–0.25).

1287. — [Nickel Anodes.] French Patent 656,475, June 26, 1928; Chem. Abs., vol. 23, 1929, p. 4152^a.

Oxides of metals of the Ni group are distributed uniformly throughout a mass of Ni in an amount of 0.25–0.5 percent of the weight of the Ni, the resulting composition being electrolytically nonpassive.

1288. — [Anodes for Electrodeposition of Nickel.] French Patent 714,869, Mar. 11, 1931; Chem. Abs., vol. 26, 1932, p. 1526.

Anodes for obtaining deposits of Ni are made. To molten Ni is added 0.002–0.0075, preferably 0.005 percent, of S and 0.1–0.2 percent of O₂ is introduced by heating or shipping the metal. The metal is cast and forged, etc., as desired.

1289. MACHU, WILLI, AND RAGHER, ADLY (Cairo University, Giza, Egypt). [The Effect of Chloride Ions on the Mechanism of the Solubility of Nickel Anodes in Sulfate Baths.] Werkstoffe u. Korrosion, vol. 5, 1954, pp. 217–222; Chem. Abs., vol. 49, 1955, p. 2903i.

In an investigation of the anodic behavior of Ni in solutions of NiSO₄, passivity was first found only in the pores of the natural covering film. On freshly polished electrodes this porosity was determined as 0.016 cm.² per cm.² of metal. By treatment in N HCl the porosity increased sharply and reached 0.10 cm.² per cm.² in sulfate baths without Cl[−] additions and 0.02 or 0.55 cm.² per cm.² with additions of 3 gm. per l. of NH₄Cl or 20 gm. per l. of NiCl₂, respectively. Surface oxides were most effectively removed by preliminary treatment in N HCl at 0.3–0.4 a. per cm.². Higher current densities caused a polishing effect. The addition of NH₄Cl and NiCl₂ partly destroyed the natural oxide film and improved the solubility of the anodes. The Cl[−] addition, on the one hand, loosened and destroyed the natural oxide film, thereby facilitating the solubility of the anodes by increasing free pore surface. On the other hand, the addition of Cl[−] led to the formation of very poor passive films, which were unstable and easily broken down.

1290. McBRIDE, S. R. (assigned to H. L. F. Co.). Apparatus for Solidifying Molten Metals in Desirable Molecular Structure (Anodes). U. S. Patent 2,148,391, Feb. 21, 1939; Chem. Abs., vol. 33, 1939, p. 3745^a.

Various structural and operative details are described of an apparatus in which a body of molten metal may be progressively solidified by feeding it downwardly through a cooled chamber while supported on a descending piston. This treatment is suitable for obtaining desired qualities in Ni anodes, bearing metals, and other metals.

1291. MOND NICKEL CO., LTD. Active Nickel Anodes. British Patent 531,671, Jan. 8, 1941; Chem. Abs., vol. 36, 1942, p. 42^a.

The anodes are made from pure nickel into which Cu, between 0.018 and 0.15 percent is introduced, and preferably between 0.03 and 0.10 percent. The anodes should also contain 0.05–0.25 percent of O₂ and 0.0015 to 0.007 percent of S. Such anodes are consistently active at any pH value up to pH 6.5.

1292. — Nickel and Cobalt Anodes. British Patent 539,180, Aug. 29, 1941; Chem. Abs., vol. 36, 1942, p. 3440^a.

A Ni anode contains C 0.15–0.35 percent, S 0.01–0.02 percent, Si 0.01–0.67 percent, and Al₂ 0.02–0.5 percent, with or without Mn, in an amount not exceeding 0.01 percent, Fe in an amount not exceeding 0.10, and Cu in an amount not exceeding 0.10 percent, the rest of the anode consisting of Ni and Co.

1293. — Production of Massive Nickel for Use as Anodes. British Patent 576,650, June 5, 1944; Canadian Patent, June 12, 1943; British Abs., 1946, p. B-I-274.

Massive Ni containing 0.005–0.5 percent of S is cathodically deposited from a Ni bath of usual composition containing at least one soluble S compound that

is reducible to H_2S at the cathode, preferably SO_2 or an alkali sulfite or acid sulfite. The tendency to brittleness of the cathode can be overcome by adding a Cu salt to the electrolyte, thus introducing 0.01–0.1 percent of Cu into the cathode. Carbon may also be incorporated in the cathode by dissolving C_2H_2 in the bath. Cathodes containing 0.005–0.03 percent of S must be heated at $815^\circ\text{--}980^\circ\text{C}$. for 20 to 30 minutes in a monoxidizing atmosphere to render them suitable for use as anodes, but if the S content is 0.03–0.5 percent, this is unnecessary.

1294. —. [Nickel Anodes for Electrolysis.] German Patent 591,373, Jan. 20, 1934 (*Cl. 48a 4*); Chem. Abs., vol. 28, 1934, p. 2281⁵.

Ni containing up to 0.25 percent of combined O is mechanically treated (for example, by rolling or hammering) at a raised temperature below its melting point. A heterogeneous Ni–NiO eutectic is obtained, which dissolves easily and uniformly in electrolytic baths.

1295. MOND NICKEL CO., LTD., AND GRIFFITHS, W. T. Active Nickel Anodes. British Patent 536,499, May 16, 1941 (addition to British Patent 531,671, Chem. Abs., vol. 36, 1942, p. 42⁵); Chem. Abs., vol. 36, 1942, p. 1552⁵.

A Ni anode having good activity and ability to corrode smoothly in solutions at relatively high pH values is made from molten commercially pure Ni containing Cu 0.018–0.15 percent, S 0.0016–0.007 percent, and free from or containing less than 0.25 percent of NiO.

1296. MOND NICKEL CO., LTD., AND PFEIL, L. B. Anodes. British Patent 581,549, Sept. 13, 1944; British Abs., 1947, p. B–142.

The anodes consist of one or more sheets of electro-deposited Ni, spot-welded together, and on or between which are fastened suspension hooks.

1297. PINNER, W. L. (assigned to Houdaille-Hershey Corp.). Nickel Anodes. Canadian Patent 392,783, Nov. 26, 1940; Chem. Abs., vol. 35, 1941, p. 1327⁵.

For use in the electrodeposition of Ni, several sheets of electrolytic Ni are connected with a dovetail joint, the joined portions being protected temporarily by a rubber band against electrolytic attack.

1298. REICHARDT, O. [New Nickel Anodes for Nickel-Plating Baths.] Chem. Ztg., vol. 60, 1936, pp. 98–99; Chem. Abs., vol. 30, 1936, p. 2852⁵.

A review of recent improvements in the manufacture of Ni anodes not easily passivated is presented.

1299. RENZONI, L. S. (assigned to International Nickel Co., Inc.). Modified Nickel Anodes. U. S. Patent 2,623,848, Dec. 30, 1952; Chem. Abs., vol. 48, 1954, p. 601.

Good corrosion characteristics over a wide range of pH (up to about 5.5) and current densities (10 to 100 a. per ft.²) for electrolytic Ni anodes is obtained by adding to them one of the following: 0.06–0.2 percent of S; 0.1–0.15 percent of S and 0.01–0.04 percent of C; 0.1–0.15 percent of S and 0.05–0.15 percent of Cu; and 0.1–0.15 percent of S, 0.01–0.04 percent of C, and 0.05–0.15 percent of Cu. The anodes are deposited from purified all-sulfate, all-chloride, or sulfate-chloride baths. The S, C, and Cu are introduced by the addition of 0.6–0.2 gm. of SO_2 per l., 0.001–0.005 gm. of C_2H_2 per l., and Cu salts to give a concentration of 0.01–0.03 gm. of Cu per l., respectively, to the electrolyte. Anodes containing only S are somewhat brittle. Their ductility is improved by the addition of C and Cu.

1300. ROEHL, E. J. (assigned to International Nickel Co., Inc.). Nickel Plating. U. S. Patent 2,504,239, Apr. 10, 1950 (*see* Chem. Abs., vol. 44, 1950, p. 2322b); Chem. Abs., vol. 44, 1950, p. 7166e.

Welded electrolytic Ni anodes may be used in electrodepositing Ni without preferential corrosion of the weld joint. The composition of the weld metal is given, and the content of the bath, which contained Ni sulfates, chlorides, and boric acid. Curves are given showing the relation of pH to chloride normality, and the anode potential of the electrolytic Ni and weld metal from pH 2.0–4.0.

1301. SPENCER, A. G. Corrosion of Nickel Anodes. Metal Ind. (London), vol. 50, 1937, pp. 141–144; Chem. Abs., vol. 31, 1937, p. 7767⁵.

The effects of the presence in Ni anodes of O, C, Fe, Si, Al, Mn, and S are discussed in relation to even solution during electroplating. The effect of insoluble material, grain size, casting, rolling and molding practice is also summarized.

1302. TEINDL, JOSEF, AND SIMKO, VILIAM. [The Rolling of Nickel Anodes.] Hornický Vestník, vol. 20, 1938, pp. 223–226; Chem. Zentralb., vol. I, 1939, p. 1052; Chem. Abs., vol. 34, 1940, p. 6906⁵.

The S content of the anodes should not exceed 0.01 percent, the C content 0.1 percent, or the Mg content 0.1 percent. The mechanical properties, production of the ingots, hot- and cold-rolling, annealing and pickling (with $\text{H}_2\text{SO}_4 + 2\text{HNO}_3$ or with 20 percent of H_2SO_4 at $60^\circ\text{--}70^\circ\text{C}$.) of the Ni anodes are discussed.

1303. THEWS, E. R. [How Can Dense Satisfactory Cast Nickel Anodes Be Prepared?] Giessereipraxis, vol. 64, 1943, pp. 169–172; Chem. Abs., vol. 40, 1946, p. 6380⁵.

The Ni must be at least 99 percent pure and contain not over 0.25 percent of Cu, 0.05 percent of Fe or Mg, 0.01 percent of Zn or Mn. Other undesirable impurities are Cr, As, Sn, C, nickel oxide, and S. Cast anodes are more soluble than rolled anodes. The melt is deoxidized with Mn or Mg. The cast anodes are forged whenever conditions require a less rapid rate of solution. In reclaiming old anodes more Mg is required for deoxidation.

1304. —. Nickel Anodes. Metal Ind. (London), vol. 71, 1947, pp. 427–429; British Abs., 1948, p. B–1–164.

The production of cast Ni anodes is described. Mg is preferred to Mn as a deoxidizer. Depolarized anodes contain 0.05–0.2 percent of O₂; more than 0.24 percent is deleterious. Rolled anodes are used in rapid plating baths to reduce slime formation. Hammered anodes, electrolytic anodes, insoluble anodes, slime formation, and anode bags are briefly discussed.

1305. —. Production of Cast Nickel Anodes. Metal Finishing, vol. 50, No. 9, Sept. 1952, pp. 70–74 and 77; Eng. Index, 1952, p. 676.

Discussed are: Effects of impurities contained in Ni anodes, and their action in electrolytes; their advantages; how to avoid the disadvantages; precautionary measures; melting of anode Ni; deoxidation; casting of anodes; their cleaning. Bibliography.

1306. TSCHOP, H. E. (assigned to International Nickel Co., Inc.). Electrolytic Manufacture of Nickel Anodes Containing Sulfur. U. S. Patent 2,392,708, Jan. 8, 1946. Chem. Abs., vol. 40, 1946, p. 2395⁵.

Satisfactory massive Ni anodes containing approximately 0.007–0.11 percent of S may be made in the electrolytic bath by introducing a S-containing additive, preferably sodium thiosulfate in concentration of 0.05–0.25 gm. per l. with the pH of the bath at 1.5–6.0. Gives detailed examples.

MOLTEN ELECTROLYSIS BATHS

1307. DROSSBACH, P. [Electrolysis of Nickel Chloride. In General.] Ztschr. Elektrochem., Ber. Bunsengesellschaft physikal. Chemie, vol. 56, January 1952,

pp. 31-35; *Metals Rev.*, vol. 25, No. 5, May 1952, p. 20 (54-C).

A method is presented of determining current yields and polarization potentials in the electrolysis of NiCl_2 mixed with molten $\text{NaCl}+\text{KCl}$. Concentration polarization resulting from diffusion is theoretically analyzed.

1308. MARSHALL, E. E., AND YNTEMA, L. F. Deposition Potentials of Chromium, Molybdenum, and Tungsten. *Jour. Phys. Chem.*, vol. 46, 1942, pp. 344-352; *Chem. Abs.*, vol. 36, 1942, p. 3435⁵.

The determination of the normal electrode potentials of these metals is complicated by their tendency to become passive in a molten AlCl_3 bath. The data found place the metals of the Cr group among those characterized by a high discharge potential. The order found, compared to Al as reference, is as follows: $\text{Fe}+0.47$, $\text{W}+0.39$, $\text{Cd}+0.36$, $\text{Mo}+0.31$, $\text{Zn}+0.24$, $\text{Cr}+0.16$ volt. Deposition potentials of Ni, Zn, and Al from fused alkali chloride AlCl_3 baths are virtually the same at 156° and 218°C .

1309. PAL'GUEV, S. F., AND SMIRNOV, M. V. Cathodic Deposition of Nickel From Molten Chloride Baths. *Jour. Appl. Chem.*, U. S. S. R., vol. 26, 1953, pp. 1107-1114 (English trans.) (*see Chem. Abs.*, vol. 48, 1954, p. 8085a); *Chem. Abs.*, vol. 49, 1955, p. 5160i.

1310. ———. [Cathodic Deposition of Nickel From Molten Chloride Baths II.] *Zhur. Priklad. Khim.*, vol. 26, 1953, pp. 1166-1175 (*see Chem. Abs.*, vol. 47, 1953, p. 6794i); *Chem. Abs.*, vol. 48, 1954, p. 8085a; *Metals Rev.*, vol. 27, No. 6, June 1954, p. 36 (100-C).

Properties of cathode deposits of Ni obtained in chloride baths strongly depend on the current density; 0.005 a. per cm^2 gives a fairly dense crystalline deposit. An increase in the current density increases the dendrites formed. The optimum current density is at 0.015 a. per cm^2 with a thickness of 0.11 mm. The character of the cathode deposit is influenced, apart from the formation of oxide films on the surface of the metal, by the nature of anion. Preliminary bubbling of HCl shows influence on deposits from chloride and phosphate baths, but not from fluoride baths.

RECOVERY OF METAL FROM IDLE PLATING SOLUTIONS

1311. PINNER, W. L. Recovery of Nickel From Obsolete Nickel-Plating Solution. *Monthly Rev.*, Am. Electroplaters Soc., vol. 29, 1942, pp. 823-830; *Chem. Abs.*, vol. 37, 1943, p. 39².

Salts from 1 million pounds of Ni or more in the United States are employed in plating baths, which are often idle and which need periodic cleaning up for fresh solutions. Attempts to recover the Ni for alloys have fallen into five classes: (1) Evaporation followed by roasting to NiO ; (2) precipitation as NiCO_3 ; (3) cementation of Ni on Fe; (4) electrolytic recovery of Ni with insoluble anodes; and (5) recovery of Ni-Fe alloys by electrolyzing with insoluble anodes. Consideration of costs, equipment and material requirements led to the adoption of the last process, which economically recovered up to 85 percent of the nickel, and which is described in this report.

1312. WESLEY, W. A., AND ROEHL, E. J. Reclaiming Nickel From Idle Electroplating Baths. *Monthly Rev.*, Am. Electroplaters Soc., vol. 29, 1942, pp. 909-917; *Chem. Abs.*, vol. 37, 1943, p. 565⁷.

The results of laboratory tests on three possible methods of recovery of Ni are presented. These are: (1) The cementation of Ni on finely divided Fe to yield an Fe-Ni powder mixture; (2) electrodeposition with insoluble anodes; (3) electrodeposition with steel anodes to produce an Fe-Ni alloy deposit. Data and

results obtained show 1 and 2 to be impracticable. Method 3 is satisfactory with regard to cost, ease of operation, and availability of equipment in the average plating plant. Results are given in sufficient detail to enable the operator to plan efficient and economical recovery of the Ni (*see Pinner, Chem. Abs.*, vol. 37, 1943, p. 39²).

1313. ——— (assigned to International Nickel Co. of Canada, Ltd.). Recovery of Nickel From Idle Nickel Electroplating Baths. U. S. Patent 2,442,628, June 1, 1948; *Chem. Abs.*, vol. 42, 1948, p. 6679c.

Ni is recovered from a Ni-containing electrolyte, such as a plating bath, by electrodeposition of a useful Ni-Fe deposit between an Fe anode and a cathode. Solution pH values between 4.0 and 5.6 are most efficient, although values as low as 2 may be used. Current densities of about 20 to 35 a. per ft^2 are employed until the Ni content of the electrolyte falls to about 3 oz. per gal. When 5 a. per ft^2 gives increased efficiency of recovery, about 90 percent of the Ni present in a typical plating bath can be recovered. United States Patent 2,442,629 is the same as United States Patent 2,442,628, except that current densities of 45 a. per ft^2 are employed when the Ni content of the electrolyte falls to about 3 oz. per gal.

FROM SCRAP RECOVERY

1314. BELL, H. M., AND SCHWEIKHER, E. W. Electrolytic Stripping Bath of Nickel Coatings From Iron Materials. U. S. Patent 2,549,411, Apr. 17, 1951; *Chem. Abs.*, vol. 45, 1951, p. 5545g.

The stripping bath is composed of NH_4NO_3 or $(\text{NH}_4)_2\text{CrO}_4$ or a mixture of CrO_3 and/or HNO_3 with organic amines in concentrations ranging from 50-300 gm. per l. at a pH of 3.0-6.0.

1315. MOHLER, J. B. (Cleveland Graphite Bronze Co., Cleveland, Ohio). Stripping Metal Overlays. *Iron Age*, vol. 159, No. 19, 1947, pp. 66-67; *Chem. Abs.*, vol. 41, 1947, p. 3733f.

Tabulated data are given for solutions to be used in stripping Ni and other metals from various base metals. In addition to the common mineral acids and alkalis, such substances as NaCN , NH_4NO_3 , FeCl_3 , CuSO_4 , acetic acid, Na_2CO_3 , H_2CrO_4 , and Na_2S are used.

1316. PASSAL, FRANK (assigned to United Chromium, Inc.). Electrolytic Method of Stripping Nickel, Chromium, Copper, Zinc, Cadmium, Tin, and Lead Electrodeposits From Ferrous Basis Metals and Compositions for Use Therein. U. S. Patent 2,561,222, July 17, 1951; *Chem. Abs.*, vol. 46, 1952, p. 842d.

Ni, Cr, Cu, Zn, Cd, Ag, Sn, and Pb electrodeposits can be stripped from ferrous basis metals by making them anodes in a bath containing 2 parts of NaNO_3 and 1 part of CrO_3 by weight, such as 200 gm. per l. of NaNO_3 plus 100 gm. per l. of CrO_3 , the pH of the solution being about 0.5. Durliron or Ni is used as cathode and the stripping is carried out, preferably with agitation, at room temperatures and $\frac{1}{2}$ -2 a. per in^2 , although temperatures from 60° - 140°F . and current densities from $\frac{1}{4}$ -4 a. per in^2 can be used. The solution functions satisfactorily even if the concentration of ingredients are 100 percent more or 50 percent less than the above values. The smoothness of the exposed basis-metal surface is not impaired by the stripping action and the exposed surface can be plated with bright or smooth deposits without any polishing.

1317. RICHARDS, E. T. [Stripping Defective Electroplate From Metallic Surfaces.] *Oberflächentechn.*, vol. 19, 1942, pp. 73-74; *Chem. Zentralb.*, vol. II, 1942, p. 2313; *Chem. Abs.*, vol. 38, 1944, p. 2572¹.

Ni is removed from Fe by anodic treatment in 67 percent of H_2SO_4 , 6 volts.

1318. SPRINGER, RICHARD. [The Recovery of Metals From Wastes.] *Ztschr. Metall-u. Schmuckwaren-Fabrik Verchrom.*, vol. 19, 1938, No. 7, pp. 11-12; No. 9, pp. 11-12; *Chem. Zentralb.* vol. II, 1938, p. 3454; *Chem. Abs.*, vol. 34, 1940, p. 2713^a.

The electrolytic recovery of Ni, Cu, brass, Cr, Zn, and Ag is critically discussed.

1319. STACK, J. R. (assigned to Nassau Smelting & Refining Co., Inc.). Refining of Nonferrous Metals. U. S. Patents 2,286,240 and 2,286,241, June 16, 1942; *British Abs.*, 1943, p. B-I-422.

Cu-bearing metal scrap containing, for example, Sn, Pb, Zn, Fe, and Ni, is cast as anodes, and these are electrolyzed in an aromatic sulfonic acid, producing Cu cathodes, an anode slime, and a fouled electrolyte. Zn and Ni are crystallized out as salts from the electrolyte, which is returned for another electrolysis step. The Ni and Zn sulfonates are boiled with CaO to yield Ca sulfonate, which is acidified to produce electrolyte for further use, and to produce nickel and zinc hydroxides. The Ni(OH)₂ is dissolved in aqueous NH₃ and the solution electrolyzed to give Ni.

1320. STARECK, J. E. (assigned to United Chromium, Inc.) Stripping Metallic Coating From Base Metals. Canadian Patent 434,632, May 7, 1946; *Chem. Abs.*, vol. 40, 1946, p. 4967^a.

Coated metal is made an anode in an alkaline aqueous solution of an alkali metal pyrophosphate at about room temperature to about 150° F. The base metal is steel or Ni and the coating metal Zn, Cu, Cd, Sn, Cr, or Mn.

1321. STUFFER, R. S. (assigned to Charles Litzenberg). Electrostripping Electrodeposited Metals. U. S. Patent 2,596,307, May 13, 1952; *Chem. Abs.*, vol. 46, 1952, p. 74431.

Cr, Ni, Cu, and other electroplates are stripped from Fe or steel bases by using the plated article as an anode in a phosphoric acid bath containing salts of one or more of the metals to be removed. The added salts facilitate the stripping action. The bath does not etch or pit the base metal, and the stripped articles are satisfactory for replating. In stripping articles with composite Cr-Ni-Cu electroplates, a solution of 1.8 lb. each of Ni²⁺, Cu²⁺, and Cr³⁺ sulfates in 225 gal. of 80 percent by volume phosphoric acid was used as the stripping bath. The articles served as the anode, and sheet Cu was used as the cathode. Composite plates, 0.001 in. in thickness were removed in 12 minutes at a current density of 1.5 a. per in.² and a bath temperature of 150° F.

1322. WHITE, C. B. Recovering Metals From Metallurgical Residues. *British Patent* 539,006, Aug. 25, 1941; *Chem. Abs.*, vol. 36, 1942, p. 3439^a.

Materials such as scrap metal, commercial residues, and metallurgical byproducts containing Cu in major amount and the metals Sn, Pb, Zn, Fe, Ni, Sb, and Ag in minor amounts are treated to separate and recover the individual metals. The materials are melted, and the molten metal is cast into anodes, which are utilized with cathodes of Cu in an electrolyzing tank containing an electrolyte consisting of an HNO₃ solution of Cu(NO₃)₂. An electric current is passed between the anodes and cathodes to dissolve the Cu, Pb, Zn, Fe, and Ni from the anodes; the Sn, Sb, and Ag separate from the anodes as a sludge, and substantially pure Cu is deposited upon the cathodes.

1323. ———. Treating Scrap Metals, etc., Containing Copper for Recovery of the Different Metals. U. S. Patent 2,200,139, May 7, 1940; *Chem. Abs.*, vol. 34, 1940, p. 5765¹.

The scrap material containing Cu in major amount with minor proportions of other metals (as Sn, Pb, Zn, Ni, and Ag), is melted and cast into anodes. Cathodes

are of Cu or other suitable metal in an electrolyte of a HNO₃ solution of copper nitrate. On passing the electric current, Cu, Pb, Zn, Fe, and Ni dissolve from the anodes, the Sn and Ag separate as a sludge, and substantially pure Cu deposits, leaving the Pb, Zn, Fe, and Ni in solution.

1324. WOHLWILL, MAX (assigned to Metallgesellschaft, A. G.). [Removal of Heavy Nonferrous Metals or Their Alloys From Coated Iron or Steel Objects.] German Patent 684,538, Nov. 38, 1939, (*Cl. 40c 1*) (addition to 679,931, *Chem. Abs.*, vol. 34, 1940, p. 330⁴); *Chem. Abs.*, vol. 34, 1940, p. 3190^a.

Objects plated with Ni or Cu are employed as anodes in a solution of a nitrate or nitrite of an alkali metal (or several such compounds) in the anode chamber of an electrolytic cell separated from the cathode member by a diaphragm; the cathode chamber is filled with a solution of the hydroxide and/or the carbonate of an alkali metal. Preferably this alkali metal is the same as that forming the cation of the nitrate or nitrite contained in the anode space.

1325. YAMANA, SANDANORI (assigned to Sumitomo Electro Industries Co.). [Recovering Scraps of Ultra-hard Alloys.] Japanese Patent 818, Mar. 31, 1950; *Chem. Abs.*, vol. 46, 1952, p. 7444d.

Scraps of WC-Co are electrolyzed by using them as the anode and Co plate or the scraps of WC-Co as cathode in a Co solution electrolyte to deposit Co at the cathode; the anode is disintegrated by heating to give WO₃.

ELECTROPLATING; SELECTED REFERENCES

1326. AMERICAN ELECTROPLATERS SOCIETY. Symposium on Nickel Plating. *Monthly Rev. Am. Electroplaters' Soc.*, vol. 33, No. 5, May 1946, pp. 494-509, disc.; Eng. Index, 1947, p. 753.

Discusses the various methods of Ni plating, including cold Ni plating and soft deposits, Watt's type Ni baths, organic bright type Ni baths, alloy-type Ni baths, all chloride Ni baths, and high-speed Ni baths.

1327. AOTANI, KAORU (Iboragi University). [Studies on Electrodeposited Alloys. I. Electrodeposited Iron-Nickel, Nickel-Cobalt, and Cobalt-Iron Alloys. 1. Change of Composition of Alloys Under Electrolytic Conditions.] *Nippon Kinzoku Gakkai-Shi*, vol. B-14, No. 5, 1950, pp. 52-55; *Chem. Abs.*, vol. 47, 1953, p. 1917a, b (see *Chem. Abs.*, vol. 47, 1953, p. 6794h).

The change in composition of the electrodeposited alloys was investigated under various electrolytic conditions, pH 2 to 5.5 current density 2 a. per dm.², time 0.4 to 4 hr., normality 1 to 2, and with or without agitation. Metal sulfates were used in the electrolyte. To make a Ni deposit simultaneously with Co or Fe, an excess of Ni in the bath is needed, since Ni is harder to deposit. It was observed that the composition of alloys was changed by pH, current density, and temperature; but, if moderate electrolytic conditions were chosen, alloys of any desired composition could be obtained.

1328. BALLAY, MARCEL. [Electrodeposition of Nickel.] *Congr. intern. élec., Paris*, sec. 7, Rapport 7, 1932, 10 pp.; *Science Abs.*, vol. 35B, p. 704 (see *Chem. Abs.*, vol. 26, 1932, p. 3732); *Chem. Abs.*, vol. 27, 1933, p. 2626.

Ballay discusses (1) slow and quick methods of Ni plating, (2) plating on Al, (3) plating on Zn and its alloys, (4) management of plating baths, (5) organization of the work, (6) repair work by thick deposits of the metal, (7) production of Ni anodes, and (8) refining of crude Ni.

1329. BEEBE, A. H. Bright Nickel Plating; a Review. *Metals and Alloys*, vol. 7, 1936, pp. 273-274; *Chem. Abs.*, vol. 31, 1937, p. 41⁵.

1330. BRENNER, ABNER, COUCH, D. E., AND WILLIAMS, E. K. Electrodeposition of Alloys of Phosphorus With Nickel or Cobalt. *Nat. Bureau of Standards, Research Paper R P 2061*, vol. 44, January 1950 *Jour. Research, U. S. Government Publications Monthly Catalog*, June 1950, item 12,297.

Alloys containing Ni or Co and as much as 15 percent of P have been electrodeposited from solutions containing phosphites. These alloys are hard and may be further hardened by heat treating at 400° C. The high-P Ni is more resistant to attack by HCl than pure Ni deposits. The high-P alloys are bright as deposited, but their reflectivity is lower than those of buffed coatings of pure Ni.

1331. BROCKMAN, C. J., AND NOWLEN, J. P. Alkaline Plating Baths Containing Ethanolamines. II. A Study of Baths Containing Triethanolamine for the Direct Nickel-Plating of Zinc. *Trans. Electrochem. Soc.*, vol. 69, 1936, 11 pp., prepr.; *Chem. Abs.*, vol. 30, 1936, p. 966¹.

The following solutions examined contained either just enough triethanolamine to give a clear solution or they contained an excess: (1) Nickel ammonium sulfate solution; (2) nickel ammonium-nickel sulfate solution; (3) nickel ammonium sulfate boric-acid solution; (4) NiSO₄ solution; (5) NiCl₂ solution; and (6) nickel ammonium sulfate-NiCl₂ solution. The plating conditions of the six solutions were determined at different temperatures, concentrations, and current densities. Current density v. electrical potential measurements were made during the plating process. Good deposits of Ni were obtained from the three sulfate baths.

1332. BROWN, HENRY (assigned to Udylite Corp.). Electrodeposition of Nickel From an Acid Bath. U. S. Patent 2,321,182, June 8, 1943; *Chem. Abs.*, vol. 37, 1943, p. 6565⁶.

For obtaining a fine-grained, lustrous, ductile deposit, a process is employed that involves electrodepositing Ni from an aqueous acid solution containing nickel sulfate or chloride or both, in the presence of an aliphatic polychlorinated or polybrominated aldehyde, such as bromal hydrate or butyl chloral hydrate soluble in the solution and having at least one halogen atom in alpha position to the aldehyde group. (*See Chem. Abs.*, vol. 37, 1943, p. 4309¹.)

1333. CHIZHIKOV, D. M., AND USTINSKII, B. Z. [Electrolysis of Nickel Sulfate in a Cell Containing An Impermeable Diaphragm; in Russian.] *Zhur. Prikladnoi Khim.* (*Jour. Appl. Chem.*), vol. 22, December 1949, pp. 1306-1309; *Metals Rev.*, vol. 23, No. 4, April 1950, p. 22 (47-c).

Experiments on the production of cathodic deposits are reported on. Electrical and compositional factors affect the electrolysis.

1334. ECKARDT, W. [Hydrogen-Free Deposits of Nickel.] *Oberflächentechn.*, vol. 12, 1935, p. 43; *Chem. Abs.*, vol. 29, 1935, p. 3239⁶.

Experiments to eliminate the harmful effects of H₂ adsorption by the basis metal led to the following bath: NiSO₄ 80 gm. per l., NiF₂ 8, NaCl 1, Na₂SO₄ 0.5, NaNO₃ 0.02, sodium phenolsulfonate 0.12, sodium citrate 2, H₃BO₃ 6, and (NH₄)₂ZrF₆ 0.2. The NH₄F combines with H₂, and the deposits adhere firmly to the basis metal.

1335. FEDOT'EV, N., AND KINKULSKII, R. [Electrodeposition of Nickel From Nickel Chloride Solutions.] *Ztschr. anorg. allgem. Chem.*, vol. 224, 1935, pp. 337-350; *Chem. Abs.*, vol. 30, 1936, p. 1308⁶.

Compact deposits of Ni can be obtained from NiCl₂ solutions without the addition of other substances.

The pH should be 6.8-6.2; the Ni concentration must not fall below 40 gm. per l.; temperature 70°-80° C. At 60° C., pH 5.0, and 40 gm. Ni l. current density 1.5 a. per dm.², the energy consumption is 2.0 kw.-hr.; with current density of 4.5 a. per dm.² the energy consumption rises to 3.5 kw.-hr.

Working of Ni ores by chlorination with subsequent electrolysis of the chloride is worthwhile; precious metals, if present in the ores, can be recovered.

1336. GRIFFITHS, W. T. American and Continental Practice in Nickel Deposition. *Metal Ind.* (London), vol. 39, 1931, pp. 443-446, 493-496, and 543-546. *Chem. Abs.*, vol. 26, 1932, p. 1197.

1337. HARFORD, C. G. (assigned to Arthur D. Little, Inc.). Electrodeposition of Metals, as for Copper, Silver, or Nickel Plating. U. S. Patent 2,355,079, Aug 8, 1944; *Chem. Abs.*, vol. 38, 1944, p. 6214².

An electrolyte is used (suitably an aqueous solution of appropriate pH) containing a compound, such as CuSO₄, AgNO₃, AgOAc or NiSO₄, of a metal having an atomic structure presenting an incomplete outer electron shell, upon ionization, and also a hydrocarbon alkyl diamine, such as ethylenediamine. Gives numerous examples, with details.

1338. INTERNATIONAL NICKEL CO., INC. (assigned to Mond Nickel Co. Ltd.). Electrodeposited Nickel. British Patent 563,101, July 28, 1944; *Chem. Abs.*, vol. 40, 1946, p. 802².

Subsequent to the addition of a deoxidant, such as B, the electroplated Ni is warmed to favor its diffusion throughout the metal structure and finally rolled to strip off the metal.

1339. KORPIUN, JOACHIM (assigned to Shering, A. G.). [Electrodeposition of Metals.] German Patent 655,146, Jan. 10, 1938 (*Cl. 48a 5*); *Chem. Abs.*, vol. 32, 1938, p. 2439⁷.

The tendency of electroplating baths to yield deposits of inferior quality after a period of use is restrained by treating the baths with a substance having a high surface to mass ratio, for example, a bleaching earth, active C, or silica gel.

1340. KÖYANAGI, S. [Electrolytic Deposition of Metals From Their Pyrophosphate Solutions.] *Bull. Chem. Soc., Japan*, vol. 10, 1935, pp. 355-356; *Chem. Abs.*, vol. 30, 1936, p. 5181⁸.

Conditions are given for deposition of Ni, Co, Cu, Zn, and Cd.

1341. KRAMER, M. D., SWANN, SHERLOCK, JR., AND BAILAR, J. C., JR. (University of Illinois, Urbana). The Electrodeposition of Cobalt and Nickel From Coordination Compounds. *Trans. Electrochem. Soc.*, vol. 90, 1946; prepr., 7 pp.; *Chem. Abs.*, vol. 41, 1947, p. 32b.

A series of cobaltic amines and one Ni ammine, with a few cobaltous amines, were studied from the point of view of their function as electroplating agents. The data suggest that the nature of the coordinating groups and the stability of the complex ions are more important than pH in determining whether good plates will be formed. Although ethylenediamine and propylenediamine complexes have equal stability, the former give much better plates than the latter, which in turn give better plates than do the complex ions of butylenediamine and stilbenediamine. This is evidently partly due to steric factors but must be explained in part on the basis of changes in the reducing potential of the metallic ions.

1342. LIND, R., HARSHAW, W. J., AND LONG, K. E. (assigned to Harshaw Chemical Co.). Electrodeposition of Metal. U. S. Patent 2,290,342, July 21, 1942; *British Abs.*, 1943, p. B-I-503.

Bright and ductile Ni plate is obtained from an acid

bath containing NiCl_2 and NiSO_4 by adding 1 to 100 mg. per l. of an azo compound containing $\text{ArN}=\text{NAr}^1$ [chrysoidine and about 0.5 gm. per l. of a naphthalene-sulfonate, or single-ring arylsulfonamide and/or sulfimide]. A suitable bath contains $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ 240, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 37.5, H_3BO_3 37.5, sodium lauryl sulfate 0.25, chrysoidine 0.01 gm. per l. and sulfonated C_{10}H_7 20 ml.; it is worked at pH 3 and 50°C . at a current density of 40 a. per ft.²

1343. MACCHIA, O. [Cobalt Plating.] *Ind. mecean.*, vol. 16, 1934, pp. 744-745; *Chem. Abs.*, vol. 29, 1935, p. 53⁹.

1344. MCQUIRE, R. C. (assigned to International Nickel Co., Inc.). Electrodeposition of Nickel. U. S. Patents 2,457,059, 2,457,060, and 2,457,061, Dec. 21, 1948; *Chem. Abs.*, vol. 43, 1948, p. 2880.

For improvement in the quality of the bond between a Ni starter sheet and the Ni deposit on it, the starter sheet is first immersed in a bath containing H_2SO_4 , NaCl , and cupric ions as in United States Patent 2,457,060; as set forth in United States Patent 2,457,060, the sheet is treated anodically in an acid, chloride bath; as stated in United States Patent 2,457,061, the sheet is treated anodically in a H_2SO_4 - CuSO_4 bath; to prevent deposition of Cu a stream of compressed air keeps it in the oxidized state.

1345. MOND NICKEL CO., LTD. Anodes for Electroplating. British Patent 539,882, Sept. 26, 1941; *Chem. Abs.*, vol. 36, 1942, p. 4034⁹.

An anode for use in Ni plating is composed wholly or predominantly of electrolytic Ni containing 0.01-0.25 percent S. The anode is formed by cathodic deposition from a bath containing 1 or more Ni salts and 1 or more sulfonic acids or sulfonates. The S and Ni are deposited simultaneously.

1346. —. Electrolytic Production of Metal Plate. British Patent 545,962, Jan. 20, 1942; Canadian Patent, Jan. 21, 1941; *British Abs.*, 1943, p. B-1-81.

The electrolyte consists of $\text{Ni}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ 25-180, aqueous NH_3 35 to 240 gm. per l., or $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ 15-75, NH_4Cl 4-20, and aqueous NH_3 35-170 gm. per l. and is operated at 10° - 20°C . (15°C . preferred) at 20-40 (25 preferred) a. per ft.². Ni anodes and a Stay-brite steel or Inconel cathode, preferably in the form of a rotating drum, are used, and the drum is lightly tapped to detach the deposit before its thickness exceeds 0.00004 in. The resulting flaky Ni is ground with stearic acid and aluminum stearate to produce a pigment for making a metal paint.

1347. PIONTELLI, ROBERTO. [Sulfamic-Acid Baths for Electroplating and Anodizing.] *Korrosion u. Metall-schutz*, vol. 19, 1943, pp. 110-113; *Chem. Abs.*, vol. 38, 1944, p. 2571¹.

Sulfamic acid is a strongly monobasic acid, crystallizing in dry state, stable, not hygroscopic, colorless and odorless, nontoxic. Ni is deposited from electrolytes prepared from 1-2M $\text{Ni}(\text{SO}_4\text{NH}_2)_2$ with 10-40 gm. per l. of free acid and a current density of over 400 a. per m.² and up to 45°C . temperature; the anodic attack is facilitated by the addition of 10 to 15 gm. per l. of NaCl . As addition agents, 10-20 gm. per l. of H_3BO_3 or 20 to 30 gm. per l. of $\text{NH}_4\text{SO}_3\text{NH}_2$ gives further improvement. Co can likewise be deposited from carbonate solutions.

1348. ROEHL, E. J., AND WESLEY, A. (assigned to International Nickel Co., Inc.). Replenishment of Nickel-Plating Electrolyte. U. S. Patent 2,541,721, Feb. 13, 1951; *British Abs.*, 1952, p. B-1-552.

The composition of an electrolyte containing NiSO_4 , 250-350 and H_3PO_4 , 20-40 gm. per l., used for Ni plating with an insoluble anode, is kept constant by circulating the electrolyte between Ni electrodes, which are dissolved anodically.

1349. SPRINGER, RICHARD. [The Use of Insoluble Anodes in Plating Baths.] *Ztschr. Metall. u. Schmuckwaren-Fabrikat Verchrom.*, vol. 18, 1937, No. 10, pp. 11-13; No. 11, pp. 11-12; *Chem. Zentralb.*, vol. I, 1938, p. 172; *Chem. Abs.*, vol. 33, 1939, p. 7205².

When insoluble anodes are used, the Ni salts must be periodically replenished in the bath. It is common practice to insert the anode into a bag or sack containing nickel carbonate. In LPW practice, scrap Ni anodes are regenerated or reactivated overnight. The current density is 2-3 a. per dm.², and the temperature 70° - 80°C . Pb alloys or Fe makes suitable insoluble anodes.

1350. WEISBERG, LOUIS. Recent History of Certain Bright Cobalt-Nickel Alloy Plating Solutions. *Trans. Electrochem. Soc.*, vol. 77, 1940, pp. 245-251, Prepr. 18; *British Chem. Abs.*, 1940, p. B-369.

Efficient purification of the electrolyte permits the Co content of the plate to be reduced from 18 percent to 1-5 percent, although 18 percent Co is still favored where maximum luster and minimum sensitivity toward the effect of impurities are required. Purification is best effected by filtration through activated C and through clay in conjunction with preferential electrolysis. The substitution of $(\text{HCO}_2)_2$ Ni and HCO_2H for HCO_2Na and a reduction in the $(\text{NH}_4)_2\text{SO}_4$ content of the bath both improve the ductility and buffing qualities of the deposit.

1351. WEISBERG, LOUIS, AND STODDARD, W. B., JR. (assigned to Weisberg & Greenwald, Inc.). Electrodeposition of Nickel. U. S. Patent 2,026,718, Jan. 7, 1936; *Chem. Abs.*, vol. 30, 1936, p. 1312².

A solution containing nickel sulfate or chloride is electrolyzed in the presence of an ammonium salt, such as the sulfate, formate of Ni or Na, and formaldehyde, which may also be used with a Co salt.

ELECTROSEPARATION

1352. AIHARA, TADASHI, SHIMATANI, TOSHIO, AND KAWAMOTO, KISSA (assigned to Besshi Mining Co.). [Electrolytic Separation of Cobalt and Nickel.] *Japanese Patent* 3705, Oct. 27, 1950; *Chem. Abs.*, vol. 46, 1952, p. 10,023a.

Sulfate solutions containing 5.8 gm. of Ni and 5.5 gm. of Co per l. are treated with 50 gm. of NH_4Cl and 50 ml. of 20-percent NH_4OH to make 5.1 of an electrolyte, which is electrolyzed by using a soluble anode (47.6 percent of Ni and 47.3 percent of Co) and a hard Pb cathode at a current density of 1 a. per cm.² for 50 hr. to give 19.5 gm. of deposit at the cathode containing 95.7 percent of Co and 3.9 percent of Ni; 20.5 gm. of the anode is consumed.

1353. BHATIA, S. L. [The Behavior of Adsorbed Electrolytes in Direct and Alternating Current Electrolysis.] *Kolloid Ztschr.*, vol. 50, 1930, pp. 55-58; *Chem. Abs.*, vol. 24, 1930, p. 2058.

The separation of CuSO_4 and NiSO_4 adsorbed on charcoal can be effected by direct current. Alternating current from the secondary of an induction coil is ineffective.

1354. BOLTON, THOMAS, & SONS, LTD., AND DOLPHIN, H. E. Separation of Copper and Nickel. *British Patent* 569,338, May 18, 1945; *Chem. Abs.*, vol. 41, 1947, p. 5036i.

Fragments of Cu scrap or metal containing Cu and Ni are caused to form the anode collectively within an apertured Pb container without a diaphragm; electrically pure Cu is separated at the cathode from a hot acid bath.

1355. BOSQUI, FRANCIS L. (assigned to Francis L. Bosqui and Rhokana Corp., Ltd.). [Ferro Cobalt.]

French Patent 759,967, Feb. 14, 1934; Chem. Abs., vol. 28, 1934, p. 3314⁴.

A mixture of alloy of Fe, Co, and Cu or other metal lower than Cu in the electrochemical series is corroded electrolytically; the Fe and Co are deposited together (*see* French Patent 759,968). A solution of the mixture or alloy is made, the solution is treated to remove Cu and then sent as catholyte in an electrolytic cell, in which the anode ions are excluded from the cathode and the acidity is below 3 gm. of H₂SO₄ per l.

1356. BOSQUI, FRANCIS L. (assigned to Francis L. Bosqui and Rhokana Corp., Ltd.). Electrolytic Separation of Cobalt Alloys. British Patent 416,256, Sept. 17, 1934; Chem. Abs., vol. 29, 1935, p. 1021⁵.

An alloy or mixture of Co and Fe containing less than 20 percent of Cu is freed from Cu in electrolytic cells with specified acidity 3-5 gm. of H₂SO₄ per l., where the Cu is thrown down as a sludge or deposited on the cathode to produce a substantially Cu-free solution. (British Patent 416,527, Sept. 17, 1934.)

As recorded in British Patent 416,528 (Sept. 17, 1934), an alloy or mixture of Cu, Co, and Fe is corroded anodically, the solution is withdrawn, and Cu is cemented on Co metal, then returned as catholyte to a second cell. Acidity is maintained at less than 3 gm. of H₂SO₄ per l. for deposition of an Fe-Co alloy.

1357. BOSQUI, FRANCIS L., AND RHOKANA CORP., LTD. [Separating Metals.] French Patent 759,475, Feb. 3, 1934; Chem. Abs., vol. 28, 1934, p. 3317⁵.

Materials containing metallic Co and Cu or materials lower than Cu in the electromotive series, particularly the alloy or mixture obtained by reducing the slag resulting from the fusion of the Cu ore, are treated to anodically dissolve this material with the electrolyte containing an excess of free acid of about 3 gm. per l. calculated as H₂SO₄. A solution of Co and of Fe, if present, is obtained, while the other metal is deposited. The electrolyte is continuously withdrawn, freed from Co and Fe, and returned to the vat with an addition of acid.

1358. CARON, M. H. [Electrolytic Separation of Pure Cobalt From a Solution of Cobalt and Nickel.] Netherland Patent 61,227, June 15, 1948 (*see* Chem. Abs., vol. 41, 1947, p. 3736h); Chem. Abs., vol. 42, 1948, p. 6679b.

In a solution containing NH₃, Ni and Co as complex NH₃ compounds, these complex ions containing Ni and Co conduct electricity. Pure Co is precipitated first, even though a larger quantity of Ni is present.

1359. ———. Elektrolytische scheiding van cobalt en nikkell. (Electrolytic Separation of Cobalt From Nickel.) Konink. Inst. van Ingenieurs-Voordrachten, Hague, Netherlands, vol. 1, No. 2, March 1949, pp. 103-123; Eng. Index, 1951, p. 783.

In the electrolytic separation of Co and Ni, a process consists in plating pure Co from electrolytes containing substantial amounts of Ni. The chemistry of the process, details of construction, and flowsheet are presented, with cathodic and anodic reactions.

1360. ———. Separation of Nickel and Cobalt. Jour. of Metals, Trans. AIME, vol. 188, January 1950, pp. 91-103; Metals Rev., vol. 23, No. 2, Feb. 1950, p. 20 (3-c).

Several chemical methods for separating Ni and Co obtained by ammonia leaching are discussed. An electrolytic method is proposed for separating the two metals from their ammonia complexes, for which the experimental procedure is detailed. The metals may also be electrolytically separated from a Ni-Co alloy.

1361. CHRISTENSEN, A. L. (assigned to International Smelting & Refining Co.). Separation and Separate Recovery of Zinc and Nickel. U. S. Patent 2,279,900,

Apr. 14, 1942; Chem. Abs., vol. 36, 1942, p. 5099²; British Abs., 1943, p. B-1-304.

A process is employed for separating and separately recovering Cu, Zn, and Ni from nonferrous secondary metal containing these metals, which involves forming, from the metal, anodes containing the bulk of the Cu and Ni and at least a small part of the Zn originally present in the secondary metal. These anodes are subjected in a H₂SO₄ electrolyte to electrolysis under such conditions that substantially pure Cu is deposited at a cathode and Zn and Ni from the anodes are dissolved in the electrolyte. A portion of the electrolyte from the electrolysis operation is periodically withdrawn and concentrated, and a mixture of Zn and Ni sulfates is crystallized from it, returning the mother liquor from the crystallizing step to the electrolysis operation. The crystallized, mixed sulfates are dried and thereafter charged into a suitable furnace and heated to a temperature and for a time sufficient to form a mixture of Ni and Zn oxides. Finely divided coke is introduced into the furnace, and the mixed oxides are heated in contact with the coke for a time and at a temperature to form and vaporize metallic Zn and to form molten metallic Ni.

1362. DE MERRE, MARCEL (assigned to Société générale métallurgique de Hoboken). Separation of Nickel From Cobalt-Containing Solutions. U. S. Patent 2,624,702, Jan. 6, 1953; Chem. Abs., vol. 48, 1954, p. 63g.

Ni is extracted from solutions containing Co and a small quantity of Ni by electrolysis with a Hg cathode at a temperature greater than 50° C. The cathode current density is adjusted so that almost all of the Ni and a small amount of Co are deposited on the Hg and form an amalgam. The amalgam is then withdrawn, and the Ni and Co in it are extracted separately by making the amalgam and anode in a 1 N H₂SO₄ solution at 75° C. and electrolyzing.

1363. DE NARBONNE, MOTAIS, AND LUCAY, A. J. [Nickel.] French Patent 667,631, Nov. 21, 1928; Chem. Abs., vol. 24, 1930, p. 1043.

Ni is separated from metals, such as Fe and Cr, by electrolysis, using as electrolyte a solution of an ammonium salt, the material to be extracted constituting the anode. The salts formed are precipitated by the ammonium salt and are held back by filters or diaphragms, while the Ni salt remaining in solution is electrolyzed and Ni is deposited at the cathode.

1364. GEORG REUTER GALVANOTECHNISCHE FABRIK. [Nickel.] German Patent 639,103, Nov. 28, 1936 (*Cl. 48a 6.05*) (addition to 638,551, Chem. Abs., vol. 31, 1937, p. 2944¹); Chem. Abs., vol. 31, 1937, p. 3799².

A citric acid electrolyte is used for electrolytic separation of Ni. A solution to prevent oxidation of the anode of Al, Mg, etc., is present in a porous container.

1365. GRIFFITH, D. L., AND RANKIN, M. J. (assigned to Hudson Bay Mining & Smelting Co., Ltd.). [Removing Cobalt From Electrolytes.] German Patent 823,791, Dec. 6, 1951 (*Cl. 40c 11*) (*see* U. S. Patent 2,471,952, Chem. Abs., vol. 43, 1949, p. 62571); Chem. Abs., vol. 49, 1955, p. 10,105d.

1366. HEGENBERG, PAUL, SCHLÖSSER, PETER, AND TAUBE, WILHELM (assigned to Silesia Verein chemischer Fabriken). [Electrolytic Separation of Metals of the Iron Group.] German Patent 692,992, June 6, 1940 (*Cl. 40c 12*); Chem. Abs., vol. 35, 1941, p. 4292⁷.

The separation is made with a Hg cathode. To prevent the Fe from adhering to the Hg and thereby reducing the overvoltage, as well as to obviate the necessity of removing small amounts of Fe from large volumes of Hg, a strong magnet is placed behind the cathode to pull the deposited Fe toward the bottom of

the cathode. This part of the cathode is removed periodically. The cathode always exposes a fresh surface, and the Hg-Fe separation is no longer costly.

1367. NORWITZ, GEO. The Ferri-Ferrous System as a Cathode Potential Regulator in the Electrolytic Separation of Silver From the Baser Elements. *Metallurgia*, Philadelphia, Pa., vol. 48, 1953, p. 47; *Chem. Abs.*, vol. 47, 1953, p. 11, 0431.

Oxidation-reduction systems such as Fe^{3+} - Fe^{2+} can prevent deposition of certain metals. The oxidation potential of this system is +0.76 volt, and as long as an excess of Fe^{3+} is present, the cathode potential cannot become more negative than +0.76 volt. Therefore, no element with a deposition potential more negative than +0.76 volt will deposit. The deposition potential of Ag is +0.80 volt. From a HNO_3 solution of Ni, Co, Fe, and several other metals and containing 5 gm. of Fe. Ag can be separated.

1368. RÖNTGEN, PAUL, AND GIESEN, KURT. [The Electrolytic Deposition of Cobalt.] *Metall. u. Erz.* vol. 39, 1942, pp. 7-13 and 28-32; *Chem. Abs.*, vol. 37, 1943, p. 6559².

The optimum conditions for electrolytic separation of Co from chloride and sulfate solutions free from Fe and Cu are: The electrolyte must be kept neutral and must contain high percentages of Co; current density, 100-200 a. per m.²; temperature, 60°-70° C.; colloidal additions of 4 mg. of glue per l. per day. In the chloride electrolysis, additions of boric acid are not absolutely necessary, but 0.5 percent of H_3BO_3 imparts high luster to the deposit. Additions of salts to the sulfate solution offer no improvements and often cause embrittlement. The free SO_4^{--} formed in the sulfate electrolysis is neutralized by adding cobalt carbonate at frequent intervals. The energy requirements were 2.34 kw.-hr. per kg. of Co in the chloride process and 2.48 in the sulfate process; the corresponding electrolytic efficiencies were 78 and 93.5 percent. Under the above conditions, the use of a diaphragm is unnecessary. The Co is deposited in the form of smooth sheets that can be easily peeled off and is 99.91 percent pure.

1369. SHIMAGAYA, YOSHIO. [Electrolytic Separation of Nickel From Cobalt by Means of a Complex Solution. I. Determination of Electrode Potentials.] *Jour. Chem. Soc., Japan, Ind. Chem. Sec.*, 1951, pp. 351-353; *Chem. Abs.*, vol. 47, 1953, p. 52761.

To aid the separation of Ni and Co by electrolyses of their ammonium complex solutions, the electrode potentials of Ni and Co were determined under various conditions; from the results the possibility of preferential deposition of Co on the cathode was considered.

1370. — (Besshi Smelter, Ehime Prefecture). [Electrolytic Separation of Nickel From Cobalt by Means of Complex Solution. II. Electrolytic Separation Under Various Conditions.] *Jour. Chem. Soc., Japan, Ind. Sec.*, vol. 54, 1951, pp. 435-437; *Chem. Abs.*, vol. 47, 1953, p. 5823h.

Electrolysis is carried out in an NH_4 complex solution of Ni and Co as electrolyte, with a C anode and hard Pb cathode. Co is preferentially deposited on the cathode surface. The approximate composition of electrolyte is NiSO_4 plus CoSO_4 , 60, NH_4Cl 60, and NH_4 20 gm. per l.; the current density is 1 a. per dm.²

1371. SUDO, KINGO (Tōhoku University, Sendai, Japan). [Electrolytic Separation of Nickel From Cobalt. I.] *Jour. Electrochem. Soc. Japan*, vol. 17, 1949, pp. 37-39; *Chem. Abs.*, vol. 48, 1954, p. 8085e.

Solutions containing NiSO_4 and CoSO_4 (1:1) were electrolyzed to determine factors affecting current density and deposited-metal purity. The following conditions favored deposition of Co: (1) Co^{++} was required in large concentrations; (2) current density was 2-3 a. per dm.²; (3) temperature had to be close to 35°

C.; (4) pH was 4-4.5; and (5) the electrolyte had to be violently agitated. The anode had to be bagged to prevent cobalt hydroxide precipitates from being stripped off.

II. Work cited above, pp. 72-74. The experiment was continued in the range of electrolyte concentration 6-18 gm. per l., Ni:Co=1:1. In this range, current efficiency and the degree of purity of Co scarcely depended on the concentration. Below 10 gm. per l. addition of NaCl improved the results, but above this concentration it spoiled them. As the Ni:Co ratio increased, the impurities in the Co deposit increased.

1372. TAKAKUWA, TOKUICHI. [Separation of Nickel, Copper, Cobalt, etc., From an Iron Alloy by Electrolysis.] Japanese Patent 2608, June 10, 1953; *Chem. Abs.*, vol. 48, 1954, p. 7462h.

An Fe-Ni (9.7 percent Ni) anode and a Pb-plate cathode in an electrolyte containing 9.5 percent of Na_2SO_4 adjusted to pH 5 with H_2SO_4 is electrolyzed (anodic current density 20 a. per dm.² and a cathodic current density 10 a. per dm.²) and 2.5 volts for 8 hr., while air is passed in below the anode and the electrolyte is kept at pH 5 with H_2SO_4 . The precipitate of $\text{Fe}(\text{OH})_3$ is separated by filtration to obtain NiSO_4 in the filtrate.

ELECTROLYSIS STUDIES PASSIVITY AND POLARIZATION PHENOMENA

1373. GRUBE, O. [Passivity of Anodes in Nickel Baths.] *Metallwaren-Ind. u. Galvano-Tech.*, vol. 28, 1930, pp. 516-517; *Chem. Abs.*, vol. 26, 1932, p. 3733.

Passivity is discussed. Passive anodes diminish the current yield and lead to the production of H_2SO_4 . Cast anodes are dissolved more readily than rolled anodes. Passivity is favored by increase in sulfate content and decrease in chloride content of the bath.

1374. HAUFFE, KARL, AND PFEIFFER, IRMTRAUD (Humboldt University, Berlin, Germany). [Passivity Phenomena With Nickel.] *Ztschr. Metallkunde*, vol. 45, 1954, pp. 554-562; *Chem. Abs.*, vol. 49, 1955, p. 745b.

Current-potential curves of thermally oxidized and polished Ni in 0.1N H_2SO_4 with and without KBr addition explain the removal of the passivity layer according to the Mott-Cabrera theory (see *Chem. Abs.*, vol. 44, 1950, p. 6366b.). Bromide ions attack both polished Ni and the passivated NiO layer. This indicates that even a pore-free NiO layer is not enough protection against halide ions. Theory and experiments are correlated. The presence of a residual passivity layer after the anodic current is stopped is demonstrated, and its resistance in 0.1N H_2SO_4 is investigated.

1375. HEYROVSKY, J. (Charles University, Prague, Czechoslovakia). Retarded Electrodeposition of Metals Studied Oscillographically With Mercury Capillary Electrodes. *Disc. Faraday Soc.*, No. 1, 1947, pp. 212-223; *Chem. Abs.*, vol. 42, 1948, p. 8677g.

An arrangement was used in which periodic current impulses charge a polarizable Hg electrode of the dropping or streaming type alternately to negative and positive potentials. The potential-time curves and derivative curves are observed on a fluorescent screen of a cathode-ray oscillograph.

Among other studies, it was found that ions of the transition elements Cr, Mn, Fe, Co, Ni, Cu, and Zn are deposited irreversibly in all solutions in which the electrode process involves a two-electron transfer. The electron acceptance of more than one electron is not simultaneous but consecutive. The second electron is acquired through dismutation, such as $2 \text{Zn}^{+} = \text{Zn} +$

Zn⁺⁺. Velocity is accelerated by heat and chloride ions and retarded by films of adsorbed molecules.

1376. HICKLING, A., AND SPICE, J. E. (University of Liverpool, England). Anodic Behavior of Metals. III. Nickel. *Trans. Faraday Soc.*, vol. 43, 1947, pp. 762-769 (*see Chem. Abs.*, vol. 39, 1945, p. 5185²); *Chem. Abs.*, vol. 42, 1948, p. 5356f.

The initial buildup of Ni anodic polarization has been determined by using the X-ray oscillograph. In solutions at pH 12-14, 2 stages in the polarization correspond to the charging of a double layer and the deposition of oxygen at the electrode. It is concluded from measurements of potentials and coulombs passed that the latter process corresponds to the formation of a layer of Ni₂O₃ greater than 1 molecule in thickness. In buffer solutions, pH 5-10, a Ni anode may become passive by the primary formation of a sparingly soluble salts film; this may be followed by formation of oxide if the film is porous. In more acid solutions the behavior is conditioned by the presence or absence of a protective film dependent on pretreatment of the electrode. All observations made conform to the film theory of passivity.

1377. KRASIL'SHIKHIN, A. I. (Institute of Nitrogen Industry of Moscow). [Air Polarization of a Nickel Cathode.] *Jour. Phys. Chem.*, U. S. S. R., vol. 21, 1947, pp. 249-254 (in Russian); *Chem. Abs.*, vol. 42, 1948, p. 2182d.

Curves of cathodic polarization of Ni in slightly acid solutions, (0.1 M K₂SO₄+0.002 N H₂SO₄) saturated with air show two horizontal sections, along which the current density is independent of applied voltage. The first section is due to diffusion of oxygen and occurs at a current density of $1-2 \times 10^{-5}$ a. per cm.² The second section is caused by catalytic liberation of H₂. Slightly alkaline solutions exhibit only the first section at a current density, which is the same for stainless steel and Fe (*see Chem. Abs.*, vol. 39, 1945, p. 2698⁹). This constant current density is determined by the rate of diffusion of oxygen. Neutral solutions (0.1 M K₂SO₄) give curves similar to those for alkaline solutions or to nearly straight lines with no detectible polarization.

1378. LITTLER, C. A., AND TARTAR, H. V. The Effect of Pressure on the Passivity of Various Metals. *Trans. Electrochem. Soc.*, vol. 74, 1938, 15 pp., prepr.; *Chem. Abs.*, vol. 32, 1938, p. 5707¹.

Anodes of Fe and Ni in H₂SO₄, Cu in HCl, and Al in HNO₃ exhibit markedly differing behaviors under reduced pressure when protected by a wax coating at the surface of the acid. The passivity of other metals is discussed.

1379. MÜLLER, W. J., AND LÖW, E. [The Theory of Passivity Phenomena. XX. The Passivity of Nickel.] *Ztschr. Electrochem.*, vol. 39, 1933, pp. 872-879; *Chem. Abs.*, vol. 28, 1934, p. 2275¹. Polemic with Georgi (*Chem. Abs.*, vol. 26, 1932, p. 5853). XXI. Film Theory. Müller, W. J. Work cited above, pp. 880-883. Polemic With Müller, E., and Schwabe, K. (*see Chem. Abs.*, vol. 27, 1933, p. 4739). Reply, Müller, E., and Schwabe, K. Work cited above, p. 884.

1380. SBORGI, U., AND BORGIA, A. [Influence of a Magnetic Field on the Passivity of Metals.] *Gazz. chim. ital.*, vol. 60, 1930, pp. 449-468 (*see Chem. Abs.*, vol. 19, 1925, pp. 3204 and 3205; vol. 21, 1927, p. 852); *Chem. Abs.*, vol. 25, 1931, p. 8.

Previous papers set forth certain relations between the electronic structure of the atoms of transition elements of the periodic system and the passivity of the metals. These relations and the facts that the transition elements are generally paramagnetic (sometimes ferromagnetic), and that the magnetic properties de-

pend upon some characteristic of the magnetic structure, point to a connection between magnetic properties and passivity. It is now shown experimentally that passivity may be interpreted electronically (*see Sborgi, Atti Soc. toscana sci. nat.*, vol. 37). Describes apparatus in detail. It was possible to obtain intense magnetization of much greater duration than with previous methods, which permitted obtaining polarization curves and time-potential curves at a constant current density. These latter are not only clearer than the polarization curves but also more reproducible. With Fe and Co (in 15 percent H₂SO₄), a distinct activating effect of magnetization was established. The Co, however, contained Fe, Cu, and Ni as impurities. With Ni the effect was much smaller, and the results varied with the samples of Ni tested.

1381. TRÜMPLE, G., AND SAXER, W. (Eidg. technische Hochschule, Zürich, Switzerland). [The Anodic Behavior of Nickel. II.] *Helv. chim. acta*, vol. 36, 1953, pp. 1630-1639 (in German) (*see Chem. Abs.*, vol. 46, 1952, p. 8991g); *Chem. Abs.*, vol. 48, 1954, p. 1178b.

The determination of the potential of Ni anodes was extended to the use of 99.995 percent pure Ni (I). The values of the critical potential of 99.5 percent pure Ni (II) (work cited) were reproduced. Whereas, the active-passive transition point of II was constant, this transition point of I fluctuated and was dependent upon previous anodic treatment. Anodes consisting of II were attacked unevenly, but I suffered severe pitting and could not be reactivated at the highest prepassive potential.

1382. TRÜMPLE, I. G., AND MEYER, H. (Eidg. Technische Hochschule, Zürich, Switzerland). [The Anodic Behavior of Nickel.] *Helv. chim. acta*, vol. 35, 1952, pp. 1304-1310 (in German); *Chem. Abs.*, vol. 46, 1952, p. 8991g.

By adjusting conditions in a cell to lessen cathode polarization and voltage drops, it was possible to retard the active passive transition in the anode. A series of experiments showed that a critical potential exists, above which passivation occurs and below which activation occurs to a limiting value independent of potential. Variation in the sulfuric acid, nickel sulfate, and nickel chloride concentrations showed that H⁺ and especially Cl⁻ shifted the critical potential to more positive values.

1383. TURNER, D. R. Anode Polarization Effects in Sulfuric Acid. *Jour. Electrochem. Soc.*, vol. 98, 1951, pp. 434-452 (*see Miller and others, Chem. Abs.*, vol. 26, 1932, p. 3171); Hedges, Protective Films on Metals, *Chem. Abs.*, vol. 31, 1937, p. 7833¹; *Chem. Abs.*, vol. 46, 1952, p. 41g.

A freshly cast anode becomes passive very quickly in 2N H₂SO₄ at 300 ma. per cm.² However, if the anode is used briefly for cathode and then returned as anode, film removed renders the anode active for a considerable time until a film again forms. The presence of chlorides tends to hinder passivation, probably through greater surface solubility at the anode.

1384. YUZA, V. A., AND KOPYL, L. D. [Oscillographic Study of the Polarization of Metallic Electrodes. III. Copper and Nickel Electrodes.] *Jour. Phys. Chem. U. S. S. R.*, vol. 14, 1940, pp. 1074-1084; *Chem. Abs.*, vol. 35, 1941, p. 3907⁸.

From experimental data on the electrodes Cu/CuSO₄, H₂SO₄, and Ni/NiCl₂, H₂BO₃ it is found that the relation between the polarization potential and the time of switching on and off is given by the equations based on the theory of delayed discharge. The polarization properties of Ni resemble those of Fe, while those of Cu resemble Zn in the nature of the oscillogram, in the change of surface of the electrode, and in the ionization constants: 10^{-10} gm.-ions per cm.² per sec. for Cu, 10^{-12} .

10^{16} for Ni. In acid solutions, NiSO_4 functions as a H_2 electrode, obeying the delayed discharge equation with a velocity constant 10^{-13} gm.-ions per cm^2 per sec.

NATURE OF DEPOSITS

1385. ACCUMULATOREN-FABRIK, A. G. Electrolytic Production of Heavy Metal Hydroxides. British Patent 305,092, Jan. 30, 1928; Chem. Abs., vol. 23, 1929, p. 4626^a.

A solution of a salt of a heavy metal—for example, a dilute nickel sulfate solution, free from foreign ions—is electrolyzed, using an anode of a heavy metal, such as Ni, or one formed from an inert material coated with a combination of the heavy metal solution during electrolysis. A current density of enough strength is used so that H_2 instead of the metal is liberated at the cathode, and the hydroxide of the metal is precipitated in the solution. Gives various details of the formation of nickel hydroxide.

1386. BRDICKA, R. [Polarographic Studies With the Dropping Mercury Cathode. XXII. Hydrolysis of Cobaltous Chloride.] Collection Czechoslov. Chem. Communications, vol. 3, pp. 406–417 (see Suchy, Chem. Abs., vol. 26, 1932, p. 43); Chem. Abs., vol. 26, 1932, p. 3443.

Current-voltage curves obtained in the electrolysis of aqueous CoCl_2 solutions showed, depending on the degree of hydrolysis, an increase in current (in the form of a "wave") at a potential of about -1.05 v., which is about 0.2 v. more positive than the deposition potential of Co. This "wave" increased greatly when the solution was heated or when a small amount of alkali was added to the solution. It disappeared entirely when the H -ion concentration was made greater than 0.0001 N. It is concluded that, at the first increase in current, Co is deposited from the hydrolytic product CoOH^+ , or from its hydrated form $[\text{Co}(\text{H}_2\text{O})_6\text{OH}]^+$, while at the second increase in current ordinary hydrated cobaltous ions $[\text{Co}(\text{H}_2\text{O})_6]^{++}$ deposit. A theoretical discussion of the experimental results and a discussion of mechanism of deposition are given.

1387. LOSHKAREV, M., GORNOSTALEVA, O., AND KRYUKOVA, A. [Cathodic Deposition of Dispersed Nickel.] Jour. Appl. Chem., U. S. S. R., vol. 19, 1946, pp. 793–800 (in Russian); Chem. Abs., vol. 41, 1947, p. 4386c.

Deposition of Ni powder was expected to take place above the limiting current density, calculated from the thickness of the double layer, the transference number, electrical conductivity, and the extracted diffusion coefficient of nickelous sulfate, $D_{\text{Ni}} = 0.24$ c a. per cm^2 , where c = moles of Ni^{++} per liter. Experiments showed that a maximum was reached at 500 a. per m^2 followed by a fall in efficiency with increasing current density. The current efficiency for compact metal falls rapidly with increasing current, being only 5 percent at 500 a. per m^2 . Increase in Ni concentration, stirring, and increase in temperature all raise the floor of current density above which powder is deposited. Addition of sulfates of other metals produced Ni deposits containing foreign metals. A cathodic polarization decrease is noted at the beginning of powder deposition, but a further rise in current density is accompanied by a slow increase in polarization.

1388. MUTA, AKINORI (Hitachi, Ltd., Tokyo). [The Low-Pressure-Discharge Electrolysis at the Interface Liquid and Gas. V. Low-Pressure Electrolysis of CoSO_4 Solution and Mechanism of Formation of Double Salts.] Jour. Electrochem. Soc., Japan, vol. 17, 1949, pp. 113–114 (see Chem. Abs., vol. 48, 1954, p. 8089e); Chem. Abs., vol. 48, 1954, p. 13,479d.

No precipitate was obtained by the discharge electrolysis of CoSO_4 solution at various concentrations. Only

a small amount of precipitate was obtained in the case of a very dilute solution. Double salts $\text{Na}_2\text{SO}_4 \cdot 10\text{Co}(\text{OH})_2$ and $\text{Na}_2\text{SO}_4 \cdot 15\text{Co}(\text{OH})_2$ were obtained by the discharge electrolysis from a mixed solution of CoSO_4 and Na_2SO_4 . The mechanism of formation of double salts was discussed, and the mechanism of the separation of Ni and Co was clarified.

1389. NENADKEVITSCH, K. A. [Electrolytic Method of Separating Nickel and Cobalt.] Compt. rend. Acad. sci., U. R. S. S., vol. 49, 1945, pp. 31–33; British Abs., 1946, p. C-I-242.

In the electrolysis of nickel and cobalt cyanide complexes, Ni can be completely deposited as black oxide on the anode if both metals can be prevented from depositing at the cathode. This can be effected by adding K_2CrO_4 or Na_2CrO_4 to the solution.

1390. NICOL, A. [Production of Cobalt Hydroxide by Electrolysis of a Solution of Sulfate.] Compt. rend., vol. 223, 1946, pp. 995–997; British Abs., 1947, p. A-I-186. Chem. Abs., vol. 41, 1947, p. 7292a.

During the electrolysis of a 0.0002 N CoSO_4 solution, a brown cathodic deposit forms, accompanied by liberation of H_2 . For concentrations up to 0.005 N, the deposit is slate-blue, becoming dark green. With 0.1 N– 1.0 N solutions the liberation of H_2 ceases, and metallic Co is deposited. The brown cathodic deposit is similar to a deposit formed on adding an excess of alkali to CoSO_4 solution. The blue variety is transformed in the medium to the green basic sulfate $\text{CoSO}_4 \cdot 3\text{Co}(\text{OH})_2$.

Hydrates were prepared by mixing cobalt sulfate with various strengths of sodium hydroxide; with weak sodium hydroxide the precipitate was $\text{CoSO}_4 \cdot 3\text{Co}(\text{OH})_2$, probably with water, and with intermediate strengths, $3\text{CoO} \cdot \text{H}_2\text{O}$.

1391. ———. [Oxide Deposits in Obtaining Metals by Electrolysis.] Ann. chim., Paris, vol. 2, 1947, pp. 670–738; Chem. Abs., vol. 42, 1948, p. 3679i.

Upon electrolysis of salt solutions with a Pt anode, Ag, Cu, and Pb appeared as metals at all concentrations; Zn, Cd, and Co only above 0.1 N; and Ni above 1 N. Below 0.002 N, silver oxide appears, while the other metals form hydroxides, detectable below 0.002 N for Cu; below 0.005 N for Co, Zn, and Pb; and below 1 N for Ni and Cd. The oxides and hydroxides obtained are more soluble in water and salt solutions than when mechanically dispersed. The existence of $\text{CoSO}_4 \cdot 3\text{Co}(\text{OH})_2 \cdot \text{H}_2\text{O}$ and $\text{ZnO} \cdot 2\text{H}_2\text{O}$ is indicated.

1392. ———. [The Formation of Nickel Hydroxide on Electrolysis of a Solution of the Sulfate.] Compt. rend., vol. 222, 1946, pp. 1034–1035; Chem. Abs., vol. 40, 1946, p. 4299⁵.

On electrolysis of N to 0.001 N nickelous sulfate solutions, nickelous hydroxide formed and dissolved in the electrolyte, at times exceeding the equivalents of Ni deposited. The current efficiency was 75–90 percent. The solubility of $\text{Ni}(\text{OH})_2$ in water and in 0.005 N and 0.001 N NiSO_4 in water was 3 mg per l. at room temperature.

1393. YOUNG, W. T., AND KERSTEN, H. A Study of Electrodeposits Containing Nickel and Sulfur. Trans. Electrochem. Soc., vol. 71, 1937, 5 pp., prepr., Chem. Abs., vol. 31, 1937, p. 611⁹.

Electrodeposits containing Ni and S were formed from an electrolyte containing essentially nickel ammonium sulfate and sodium thiosulfate. The composition of the deposits was found to depend on the current density and ranged from about 27 percent of S and 72 percent of Ni to 8 percent of S and 87 percent of Ni. Four different structures were observed: Nearly pure Ni_3S_2 ; the same plus an unknown structure; an amorphous structure; and a poorly crystalline Ni structure.

OVERVOLTAGE, VOLTAGE, AND DISTRIBUTION OF CURRENT

1394. ESSIN, O., AND LOSCHKAREV, M. [Potential Balance in Fainshtein's Electrolytic Nickel-Refining Process.] *Jour. Appl. Chem., Russia*, vol. 11, 1938, pp. 1432-1439; *British Chem. Abs.*, 1939, p. B-619.

The fall in potential at different parts of the vat, involved in Fainshtein's process, consisting in electrolysis in the system Ni cathode|NiSO₄, H₂BO₃, H₂O||NiSO₄, H₂BO₃, H₂SO₄, H₂O|Ni anode at 60° C. (calculated at cathode 150 a. per m.²) is determined.

1395. GEORGI, KONRAD. [The Anodic Behavior of Nickel.] *Ztschr. Electrochem.*, vol. 38, 1932, pp. 681-688 and 714-731; *Chem. Abs.*, vol. 26, 1932, p. 5853.

From a comprehensive study of the behavior of Ni anodes in N solutions of NiCl₂, NiBr₂, Ni(ClO₄)₂, and Ni(H₂PO₄)₂, at various pH values and temperatures and with various surface conditions, it is concluded that the theory of Müller (*Chem. Abs.*, vol. 26, 1932, p. 3171) applies, with the assumption of a saturation current or a superoxide film.

1396. ———. [The Anodic Behavior of Cobalt.] *Ztschr. Electrochem.*, vol. 39, 1933, pp. 209-219; *Chem. Abs.*, vol. 27, 1933, p. 4486.

The influence of the current density, anion, pH, and temperature on the anodic behavior of Co was investigated and is compared with corresponding measurements for Ni (*Chem. Abs.*, vol. 26, 1932, p. 5853).

1397. ———. [The Anodic Behavior of Nickel. III.] *Ztschr. Electrochem.*, vol. 39, 1933, pp. 736-743 (*see Chem. Abs.*, vol. 26, 1932, p. 5853); *Chem. Abs.*, vol. 27, 1933, p. 5650.

In the passage from the active to a more noble state, the diminution of the H-ion in the diffusion layer is involved; from a higher potential on, perhaps the formation of oxide layers on the most soluble spots is also effective. Completion of the oxide layer prevents further Ni formation and increases polarization.

1398. ———. [The Anodic Behavior of the Iron Metals.] *Korrosion u. Metallschutz.*, vol. 9, 1933, pp. 302-307 (*see Chem. Abs.*, vol. 27, 1933, p. 5650); *Chem. Abs.*, vol. 28, 1934, p. 974².

Presents theoretical discussion of the potential phenomena with Fe, Ni, Co anodes based on the assumption of adsorbed layers on the surface is presented.

1399. HICKLING, A., AND SALT, F. W. Studies in Hydrogen Overvoltage at High Current Densities. V. The Decay of Hydrogen Overvoltage. *Trans. Faraday Soc.*, vol. 37, 1941, pp. 450-462 (*see Chem. Abs.*, vol. 35, 1941, p. 2797⁶); *Chem. Abs.*, vol. 36, 1942, p. 350¹.

A new method (*see Chem. Abs.*, vol. 34, 1940, p. 3596⁷) permitting observation from a minimum time of 5×10^{-6} seconds was employed to follow the decay of H₂ overvoltage upon interruption of the polarizing current. Wires or rods, and also thin electrodeposited films on Cu of many metals, including Ni, were used.

1400. HUNT, HERSCHEL, CHITTUM, J. F., AND RITCHEY, H. W. Overvoltage. *Trans. Electrochem. Soc.*, vol. 73, 1938, 15 pp., prepr.; *Chem. Abs.*, vol. 32, 1938, p. 862⁷.

The overvoltage of H₂ was measured on Ni and a number of other metals; likewise the overvoltage of O₂ on Pt and Au in KOH solutions. Colloidal metals changed the overvoltage. Rotation of the electrode decreased overvoltage. At current densities from 10^{-4} – 10^{-3} ma. per cm.², the overvoltage on bright metals was less than the reversible potential; also by adjustment of finely divided metal on electrode surfaces, the overvoltage for various metals became nearly the same.

1401. LEGRAN, A., AND LEVINA, S. Hydrogen Overvoltage on Nickel in Solutions of Acids. *Acta physicochim.*, U. R. S. S., vol. 12, 1940, pp. 243-252 (in English) (*see Chem. Abs.*, vol. 34, 1940, p. 1256⁴); *Chem. Abs.*, vol. 34, 1940, p. 7757⁸.

The eta-log *i* curves, where eta is overvoltage and *i* the current density, in H₂SO₄, HCl, and HBr solutions are initially horizontal and then obey Tafel's equation $\eta = a + b \log i$ with $b = 0.093$ – 0.103 without obtaining a "saturation-current" value. The eta values are virtually the same in all three acids; no adsorption of Cl or Br ions on Ni is observed; delta eta is about 58 mv. for C₁:C₂=10:1 from C=1 N down to C=0.01 N and decreases at lower concentrations.

1402. LOSHKAREV, M., AND LAPP, G. (Ural Industrial Institute, Kirovo). [Voltage Distribution in Nickel-Refining Baths.] *Jour. Appl. Chem., U. S. S. R.*, vol. 18, 1945, pp. 405-411; *Chem. Abs.*, vol. 40, 1946, p. 4961².

The voltage distribution was studied in commercial baths for Ni refining of Cu-Ni alloy (3 percent Cu) at 135 a. per m.² cathode current density. The results are given graphically. It is shown that, at a current density of 200–250 a. per m.² and with the same current efficiency as at 135 a. per m.², the electric conductivity of the electrolyte must be increased 1.6–2.1 times, achievable by addition of 60–80 gm. per l. of Na₂SO₄.

1403. LUKOVTSY, P., AND LEVINA, S. [Hydrogen Overvoltage of Nickel in Alkaline Solutions.] *Jour. Phys. Chem., U. S. S. R.*, vol. 21, 1947, pp. 599-612 (in Russian); *Chem. Abs.*, vol. 41, 1947, p. 6820i.

The slopes $d\eta/di$ of the curve of overvoltage against current density are almost identical for Ni rods and plates in different positions. The overvoltage on Ni, eta appears to be an inverse function of sodium hydroxide concentration, increasing with diminishing alkali concentration. The capacity of a Ni electrode calculated from the rate of decay of eta after the current is switched off, is greater in the last stages of decay. It is greater with greater hydroxide concentration and initial overvoltage.

1404. LUKOVTSY, P., LEVINA, S., AND FRUMKIN, A. [Hydrogen Overvoltage on Nickel.] *Jour. Phys. Chem., U. S. S. R.*, vol. 13, 1939, pp. 916-930 (*see Chem. Abs.*, vol. 34, 1940, p. 1256⁴); *Chem. Abs.*, vol. 34, 1940, p. 4672⁸.

1405. ———. Hydrogen Overvoltage on Nickel. *Acta physicochim.*, U. R. S. S., vol. 11, 1939, pp. 21-44, (in English); *Chem. Abs.*, vol. 34, 1940, p. 1256⁴.

The hydrogen overvoltage on Ni in HCl solutions from 0.0006–0.15 N and for current densities from 10^{-5} – 10^{-4} a. per cm.² obeys Tafel's equation $\eta = a + b \log i$, with $b = 0.100$. In NaOH concentrations from 0.001–8.8 N, $b = 0.108$ to 0.115 at 20° C. In acid solutions, the overvoltage increases on addition of neutral salts; in alkaline solutions it decreases. A saturation current similar to that predicted by Horiuti and Okamoto (*Chem. Abs.*, vol. 32, 1938, p. 4861⁹) was observed only at much higher current densities.

1406. MANTZELL, E. [Current Distribution in Electrolytes. II. Nickel Baths.] *Ztschr. Electrochem.*, vol. 43, 1937, pp. 174-186 (*see Chem. Abs.*, vol. 30, 1936, p. 7046⁵); *Chem. Abs.*, vol. 31, 1937, p. 5687⁵.

The practical factors in operating Ni electrodeposition baths are treated. In baths of normal Ni concentration and high pH, polarization and conductivity are the determining factors in "throwing power"; addition of salts to increase conductivity has a negligible effect on current efficiency. High temperature and high Ni-ion concentration make for poor distribution of current. The addition of good conducting salts and use of low current density is recommended.

1407. MÜLLER, ERICH, AND JANITZKI, J. [The Electromotive Behavior of Nickel and Cobalt.] *Ztschr. Physikal. Chem.*, vol. A-162, 1932, pp. 385-397 (see *Chem. Abs.*, vol. 26, 1932, p. 4527); *Chem. Abs.*, vol. 27, 1933, p. 887.

Co and Ni behave in the same way as previously described for Fe. In neutral metallic salt solutions, it is doubtful whether Ni ever attains a reversible potential. For Co in $N\text{CoCl}_2$ solution, the reversible potential is -0.292 volt.

1408. NEWBERRY, EDGAR (University of Cape Town, Union of South Africa). Reversible Overvoltage. *Trans. Faraday Soc.*, vol. 43, 1947, pp. 127-138; *Chem. Abs.*, vol. 41, 1947, p. 5033c.

Electrodes of Ni and Co, among others, were investigated, using an improved form of cathode-ray oscillograph; this study showed that the total opposition to the passage of current between electrode and electrolyte when a gas is liberated consists of two parts—a reversible and an irreversible one. Due to gas-film resistance, the irreversible part is governed by (1) the mechanical nature of electrode surface, a rough surface allowing easier escape of gas, and less electrical resistance, and (2) by the current density; a high current density allows less polarization. The reversible part is made up of four factors: (1) Concentration polarization, (2) back ionization of deposited gas, (3) back ionization of electrode, and (4) back ionization of overvoltage compounds of gas with electrode metal.

1409. REISER, H. J., AND FISCHER, H. (Technische Hochschule, Karlsruhe, Germany). [An Analysis of the Voltage Curves for the Simultaneous Separation of Hydrogen and Nickel.] *Ztschr. Elektrochem.*, vol. 58, 1954, pp. 668-672; *Chem. Abs.*, vol. 49, 1955, p. 5159f.

The simultaneous separation of H_2 and Ni from 3 M $NiCl_2$ solution in M HCl was studied with twin cathodes, current densities of 10^{-1} – 10^{-3} a. per cm^2 and temperatures of 20° – 50° C. The partial current-voltage relations for both H_2 and Ni were discussed. In the H_2 release, the rate determining step was the catalytic combination of H to H_2 . The deposited Ni had catalytic activity. Anthranilic acid was used to complex $Ni(OH)_2$, to permit a study of the colloidal $Ni(OH)_2$; inhibition during electrolysis.

1410. SALT, F. W. Overvoltage in Metal Deposition and Solution. I. Nickel. *Disc. Faraday Soc.*, No. 1, 1947, pp. 169-181; *Chem. Abs.*, vol. 43, 1949, p. 5674d.

The course of decay of polarization at a Ni electrode in electrolytes of varying composition and pH is discussed.

1411. SCHMID, GERHARD, AND STOLL, E. K. [The Overvoltage of Hydrogen in Alkaline Electrolytes at Reduced Pressures.] *Ztschr. Electrochem.*, vol. 47, 1941, pp. 360-368 (see Bircher and Harkins, *Chem. Abs.*, vol. 18, 1924, p. 494; Knobel, *Chem. Abs.*, vol. 19, 1925, p. 1369; Cassel and Krumbein, *Chem. Abs.*, vol. 29, 1935, p. 1017⁹); *Chem. Abs.*, vol. 35, 1941, p. 6516⁵.

The hydrogen overvoltage has been measured at cathodes of Cu, Ni, and other metals at 0° C. in 0.1 N NaOH at current densities of 10^{-4} – 10^{-2} a. per cm^2 and at pressures from 1 atm. down to 15 mm. of mercury. An equation relating overvoltage to pressure is derived. The conclusion reached is that the rate of discharge is the important factor, that of the reverse process (for example, the conversion of H_2 gas into ions) being negligible in comparison.

1412. SHRIVASTAVA, HIRALAL. Physicochemical Studies With Aqueous Fluoride Solutions. II. Hydrogen and Oxygen Overvoltages in Hydrofluoric Acid.

Proc. Indian Acad. Sci., vol. 26A, 1947, pp. 167-177; *Chem. Abs.*, vol. 42, 1948, p. 2183h.

Using a number of metals, among which were Ni and Co, H_2 overvoltages were determined in 0.2 N hydrofluoric acid and on Pt in stronger concentrations of hydrofluoric acid, sulfuric acid, and formic and acetic acids at various current densities.

1413. VERDIECK, RALPH, KSYCHI, SISTER M. J., AND YNTEMA, L. F. The Deposition Potentials of Cobalt, Nickel, and Copper From Chloride and Bromide Solutions. *Trans. Electrochem. Soc.*, vol. 80, 1941, 13 pp., prepr.; *Chem. Abs.*, vol. 35, 1941, p. 6192⁹.

The deposition potentials in solutions containing from 0-9 mol. percent of $MgCl_2$ or $MgBr_2$ were measured at 30° C. Similar measurements were made at temperatures up to 90° C. on solutions of the metallic halides containing 9 mol. percent of Mg halides. Co and Ni are deposited most easily from hot solutions containing a high concentration of halide ion. The deposition of Cu is also discussed.

1414. YAMAMOTO, YOITI. [Electrode Potentials of Metals and Alloys in Nitric Acid and Copper Nitrate Solution.] *Bull. Inst. Phys. Chem. Research (Tokyo)*, vol. 17, 1938, pp. 614-641 and 680-693; *Chem. Abs.*, vol. 33, 1939, p. 6169⁹.

The single-electrode potential for Ni, Co, and a large number of elements (and alloys) in HNO_3 was determined by using the vacuum-tube potentiometer. A relation between atomic number and electrode potential was found, but the potential was not always proportional to the rate of attack. Potential series after 20 minutes immersion are given for 8 concentrations from 0-60 percent of HNO_3 , and also in 2-20 percent of $Cu(NO_3)_2$.

MISCELLANEOUS STUDIES

1415. KHEIFETS, V. L., AND ROTINYAN, A. L. (A. A. Zhdanov State University, Leningrad). [Simultaneous Discharge of Ions and the Theory of Electrolytic Refining of Metals.] *Doklady Akad. Nauk., S. S. S. R.*, vol. 82, 1952, pp. 423-426; *Chem. Abs.*, vol. 46, 1952, p. 6524i.

The theory of simultaneous discharge is given for conditions where the rate of discharge of one kind of ion is considerably greater than that of ions for the other kind. The expression derived was verified by an experimental electrolysis depositing Ni from a bath containing nickel sulfate, sodium sulfate, sodium chloride, and boric acid, with additions of Cu, Co, and Zn. In another experiment, various amounts of Mn^{++} were added to solutions of several Ni concentrations, where the rate of codeposition of Mn was determined by its rate of discharge; the Mn content in the deposit decreased with increasing Ni-ion concentration in the solution and increased with the current density. Absorption of anions was found to improve the purity of deposits.

1416. KUDRA, O. K., GITMAN, E. B., AND SHILAK, N. S. (Inst. Gen. Inorg. Chem. Acad. Sci. Ukraine S. S. R., Kiev). [Relation Between Concentration, Current Density, and Time in Electrodeposition of Cobalt.] *Ukraine Khim Zhur.*, vol. 16, No. 5, 1950, pp. 484-491; *Chem. Abs.*, vol. 47, 1953, p. 12,053i.

The relation of these three factors was studied on cobaltous chloride, cobaltous acetate, and cobaltous sulfate. As in previous studies with other metals, the values $it^{0.5}$, where i is current density and t the lapse of time to the appearance of black loose deposit, were constant for any one concentration, $C = ait^{0.5}$. Plotting $it^{0.5}$ against C , concentration, produced straight lines through the origin.

1417. MÜLLER, W. J. [Anodic Behavior of the Iron Metals.] *Korrosion u. Metallschutz*, vol. 10, 1934, pp. 1-5 (*see* Polemic with Georgi, *Chem. Abs.*, vol. 28, 1934, p. 974⁸); *Chem. Abs.*, vol. 28, 1934, p. 2275².
1418. PIONTELLI, ROBERTO, AND SIMONETTA, MASSIMO. [The Behavior of Metals in Concentration Cells.] *Gazz. chim. ital.*, vol. 78, 1948, pp. 424-429; *Chem. Abs.*, vol. 43, 1949, p. 8286e.

The previous classification of metals into normal metals and metals with electrochemical inertia according to their behavior as salts in aqueous solution and under other conditions (*see* P. Comm. XI Congr. intern. chim., London, July 1947; *Chem. Abs.*, vol. 43, 1949, p.

7351e,h; Schuyten, *Chem. Abs.*, vol. 42, 1948, p. 90f) is used as a basis for studying the behavior of metals in concentration cells, that is, in galvanic chains of the type: $M|MX_{\alpha\beta}\cdot(C_1)||MX_{\alpha\beta}\cdot(C_2)|M$. The behavior of Cu and Ag is reported on. In continuation, the behavior of 3 representative metals—Sn, Pb, and Cd—and 2 inert metals—Fe and Ni—was studied. The results of the present and previous work show that metals of all three groups behave in accordance with what was to be expected on the basis of the atomic structures of metals and other theoretical considerations and that the effect of the anion is appreciable, particularly in the part it plays in the phenomena of anodic and cathodic polarization.

PART V. MISCELLANEOUS

RECOVERY AS A BYPRODUCT IN ZINC METALLURGY

1419. AGEENKOV, V. G., AND TZAGIKYAN, E. A. [Removal of Cobalt From Solutions in the Electrolytic Production of Zinc.] *Tsvetnye Metal*, vol. 9, 1934, pp. 113-124; *Chem. Abs.*, vol. 29, 1935, p. 4711⁶.

A series of experiments was carried out to prove the possibility of precipitating Co from a solution of $ZnSO_4$ by means of Zn powder, in the presence of As and Te, and to determine the optimum conditions therefor.

1420. BUDON, V. D., AND GROMOV, B. V. [Removal of Cobalt From Zinc Sulfate Solutions.] *Russian Patent* 65,696, Jan. 31, 1946; *Chem. Abs.*, vol. 40, 1946, p. 7538⁶.

Co is precipitated from zinc sulfate solutions by an alkali xanthate in the presence of a small quantity of bivalent Cu to hasten the oxidation of Co. The Co content in zinc sulfate solutions can thus be reduced from 100 gm. per m.³ to 2-5 gm. Any As, Sb, is also precipitated, together with the Co.

1421. CAMBI, LIVIO. [Cobalt in the Electrowinning of Zinc From Its Ores: Refining and Recovery of Electrolyte.] *Chim. e ind. (Italy)*, vol. 21, 1939, pp. 257-264; *Chem. Abs.*, vol. 33, 1939, p. 7667⁶.

Co can be recovered from mother liquors in the electrolytic production of Zn by means of xanthate, $Co(MeOCS_2)_2$, which is insoluble as well as very stable. Co can be recovered from this complex in a way similar to its recovery from alpha-nitroso-beta-naphthol, by carbonization.

1422. ———. [Cobalt in the Electrolytic Treatment of [Zinc] Blende.] *Atti X^o Congr. intern. chim.*, vol. 3, 1939, pp. 546-554; *Chem. Abs.*, vol. 33, 1939, p. 9148¹.

Two methods are described for removing and recovering Co from solutions of some Italian Zn minerals in H_2SO_4 . In an inorganic method, Co and other impurities are precipitated by the addition of $CuSO_4$ and As_2O_3 , and by a double treatment with Zn dust, at a temperature above 75° C. This precipitate is then treated further with dilute acid and Zn dust to recover Co. In an organic method, alpha-nitroso-beta-naphthol is used at room temperature to form a complex with the Co present, which is then extracted with benzene. This complex is then ashed and the residue dissolved in acid for further fractionation of the Co.

1423. ENZFELDER, H. [The Purification of Technical Zinc Sulfate Solutions by Cementation.] *Berg.-u. hüttenmänn. Monatsh., Montan. Hochschule, Leoben*, vol. 98, 1953, pp. 227-234; *Chem. Abs.*, vol. 38, 1954, p. 3646g.

Some impurities that interfere with electrodeposition of Zn can be precipitated as hydroxide by hydrolysis, for example, Fe, Al, SiO_2 , As, Sb, Ge, and, in part, Ni and Co. Further purification is effected principally by Zn dust. Experiments were made to determine the effects of rate of stirring, of temperature, and of metal concentration on cementation and to determine the minimum quantity of Zn dust required. In the presence of various metals in various concentrations, the quantity of Zn dust required for precipitating all of the metals is determined by the amount of metal most difficult to remove. Ni is precipitated only from the hot

solution; large quantities of Cd are best precipitated in the cold.

1424. GETSKIN, L., AND ROZOV, V. [Elimination of Cobalt in Electrowinning of Zinc.] *Tsvetnye Metal*, vol. 15, No. 10/11, 1940, pp. 78-82; *Chem. Zentralbl.*, vol. 1, 1942, p. 1933; *Chem. Abs.*, vol. 37, 1943, p. 4971⁶.

The Co content of the Zn concentrate was 0.004-0.02 percent; in the electrolyte it amounted to as much as 55 mg. per l. The removal of the Co from the electrolyte occurred after the removal of Cu and Cd and was brought about by means of beta naphthol and $NaNO_2$. The N_2 content of the Co-free electrolyte was about 15 mg. per l., in the form of ammonium salts.

1425. GILL, A. S. (Electrolytic Zinc Co. A'asia Ltd. Risdon, Tasmania). Production of Cobalt Oxide, Cobalt Sulfate, and Electrolytic Cobalt. *Proc. Australasian Inst. Min. and Met.*, vol. 152-53, 1949, pp. 73-83; *Chem. Abs.*, vol. 46, 1952, p. 5274h.

Plant and processes are described for preparing Co_3O_4 , $CoSO_4$, and electrolytic Co at Risdon from the precipitate of cobalt nitroso-beta-naphtholate separated during the purification of the $ZnSO_4$ electrolyte. The pulped precipitate is treated with H_2SO_4 , the gypsum formed separated by flotation, Zn washed out by displacement, and the residue fired to oxide; about 15 tons per year is produced. The cobalt oxide is mixed with H_2SO_4 , fired in a reverberatory furnace, cooled, leached with H_2SO_4 , neutralized with limestone, and cobalt sulfate heptahydrate crystallized out, about 1-1½ tons per month being produced. In producing electrolytic Co, iron hydroxide is precipitated and removed, Zn and Cu removed by H_2S , and the solution electrolyzed to exhaustion with steel cathodes and Pb-Ag anodes. Details are given.

1426. GREVEL, ADELBERT. [The Precipitation of Cobalt From Zinc Sulfate Solutions in the Electrolytic Production of Zinc.] *Wiss. Veröffentlich. Siemens-Konzern*, vol. 13, No. 1, 1934, pp. 61-71; *Chem. Abs.*, vol. 28, 1934, p. 3665⁶.

The potential of Zn plate and Zn powder on Pt in a stirred Zn solution at 70° C. containing 10 percent Zn was measured against a 1 N calomel electrode. The addition of copper or cadmium sulfate did not affect the e. m. f., while the addition of iron, cobalt, or nickel sulfate resulted in slow change to a more positive e. m. f. after 90 minutes. The addition of compounds is discussed.

1427. GRIFFITH, D. L., AND RANKIN, M. J. (assigned to Hudson Bay Mining & Smelting Co., Ltd.). Process for Removing Cobalt From Electrolytes. U. S. Patent 2,471,952, May 31, 1949; *Chem. Abs.*, vol. 43, 1949, p. 6527i.

For successful removal of Co from electrolytes in the refining of Zn, Sb in the form of the oxide or as tartar emetic, in an amount 4-10 times the Co present, should be added to the electrolyte. The solution should further contain about 0.5-1.5 gm. per l. of Cu. The addition of Zn dust or other precipitating agent will then remove all of the Co and leave but 0.016-0.020 mg. per l. of Sb.

1428. ——— (assigned to Hudson Bay Mining & Smelting Co., Ltd.). Removing Nickel and Cobalt Impurities From Zinc Electrolyte Solutions. U. S. Patent 2,509,916, May 30, 1950; *Chem. Abs.*, vol. 44, 1950, p. 7679e.

Small amounts of Ni and Co, which are difficult to remove from electrolytes by cementation, can be thrown out by the addition of small amounts of As and Tl in the presence of Cu salts. It was found that 25 mg. of Tl and 175 mg. of As per l. in the presence of Zn, Cu salt and with 1 hr. agitation at 40° C., reduce Co from 23.6 mg. per l. to 1.2 mg. per l. and Ni from 18.8 mg. per l. to a point where it is no longer detectable. (United States Patent 2,509,917.) The same as the foregoing, except that, in place of Tl, 100 mg. per l. of Pb is used. (United States Patent 2,509,918.) Same as above except that in place of Tl or Pb, 250 mg. per l. of As is employed.

1429. GROMOV, B. V., AND PASTUKHOVA, A. D. [Purification of Zinc Sulfate Solutions: Eliminating Cobalt as Xanthate.] *Tsvetnye Metal*, vol. 19, No. 3, 1946, pp. 21-28; *Chem. Abs.*, vol. 41, 1947, p. 2338i.

The method is an adaptation of the Cambi method (*Chem. Abs.*, vol. 33, 1939, p. 7667^a). Co, present in solutions of ZnSO₄ in the bivalent state, is oxidized to the trivalent state and precipitated with potassium butyl-xanthate. The oxidation is by air in the presence of Cu acting as O carrier. The precipitation is carried out at pH 5.5-5.6, adjusted by adding CaO or ZnO to raise the pH. CuSO₄ (approximately 40 mg. per l.) is supplied in the form of the overflow from a Dorr thickener in the Zn refinery. The optimum temperature is 38°-40° C. The needed ratio of xanthate to Co is 23:1. Zinc sulfate solutions containing 30-35 mg. per l. of Co were freed of an average of 87 percent of the Co.

1430. HÄNSEL, GÜNTHER. [The Precipitation of Cobalt From Zinc Sulfate Solutions by Means of Zinc Dust Mixed With Metal Compounds.] *Wiss. Veröffentlich. Siemens-Konzern*, vol. 13, No. 1, 1934, pp. 55-60; *Chem. Abs.*, vol. 28, 1934, p. 3665^e.

As is well-known, slight amounts of Co exert a detrimental effect on the electrolytic deposition of Zn from H₂SO₄ solution. To precipitate the Co, Zn dust mixed with compounds of Cu, Bi, Cd, Ag, Hg⁺, Pb, Sn⁺⁺, and Sn⁺⁺⁺ was added to the stirred solution at 80° C. Only SnSO₄, and to a lesser extent, Sn(SO₄)₂, were effective. Six successive additions of Zn dust (0.83 gm. per l.) mixed with Sn as SnSO₄ (0.5 gm. per l.) over a period of 3 hr. reduced the Co content from 70 to 1.9 mg. per l. Comparison with admixed As as As₂O₃ and Sb as tartar emetic indicated a higher precipitation efficiency for SnSO₄.

1431. HILL, C. T. (assigned to The Pyrites Co., Ltd.). Recovery of Copper, Zinc, and Cobalt. *British Patent* 591,801, Aug. 28, 1947; *Chem. Abs.*, vol. 42, 1948, p. 1178i.

In solutions where the Zn and Co are to be recovered subsequent to Cu recovery, the introduction of Fe during Cu removal must be avoided. To recover the dissolved Cu, stir metallic Cu into the solution which should contain a slight excess of Cl ion. Filter off the precipitated CuCl, add acid, and precipitate metallic Cu from the acidified sludge by bringing it into contact with metallic Fe. Part of the recovered Cu is recycled, and the rest is available for other use. To the filtrate from the CuCl separation, add Cl₂ gas and then Na₂CO₃ slowly until the pH reaches 5.8 whereby traces of Cu, Fe, Mn, Pb, and Ag are precipitated and discarded. The solution then contains only Zn, Co, and Ni. To recover the Co, heat to 40°-60° C., add a soluble alkali and then Cl₂ gas, reduce the pH to 3.5, whereby Zn and Ni are redissolved and Co remains as precipitate. Zn is usually not profitably recovered if Ni is also present.

1432. LYUBCHENKO, V. A. [The Production of Electrolytic Zinc.] *Tsvetnye Metal*, vol. 13, No. 9, 1938, pp. 77-90; *Chem. Zentralb.* vol. I, 1939, p. 3445; *Chem. Abs.*, vol. 34, 1940, p. 7754^a.

Redesign and improvement in operation of roasting furnaces, and improvements in the complete elimination of impurities of Fe, Cd, and Co from the Zn electrolyte are discussed.

1433. ROSS, S. W. The Purification of Zinc Sulfate Solutions Intended for the Electrolytic Recovery of Zinc. *Proc. Australasian Inst. Min. Met.*, vol. 95, 1934, pp. 167-199; *Chem. Abs.*, vol. 29, 1935, p. 3954^e.

According to the electrochemical series, Co should be precipitated by Zn metal, but cobaltic sulfate is only slightly ionized in the presence of so much Zn, and the reaction is very slight; Co may be removed by using a powerful oxidizing agent, but since Mn is preferentially oxidized, the expense is considerable; in the presence of Cu and As, Zn will remove Co, but here the As formed is injurious to health; the most satisfactory method of purification involved addition of a nitrosonaphthol to precipitate Co.

1434. SCHERESCHESKY, P. L. Zinc Metal. *U. S. Patent* 2,685,506, Aug. 3, 1954; *Chem. Abs.*, vol. 48, 1954, p. 11,284f.

An apparatus and method of operation are described in which the main operation is reduction of the ore to zinc metal, with simultaneous recovery of Pb, Cu, Ni, and Ag.

1435. SEQUINE, WILLIAM, AND ZWEYER, JOHN, JR. (assigned to Glidden Co.). Metallurgy of Zinc Fumes, etc. *U. S. Patent* 2,264,337, Dec. 2, 1942; *Chem. Abs.*, vol. 36, 1942, p. 1581^a.

A byproduct fume or other powdery material containing organic matter and Zn, Pb, Sn, Cd, Ni, Cu, As, Sb, and Cl compounds is treated with water to form coarse particles which are roasted to burn away organic material and volatilize chlorine compounds, and the roasted product is then subjected to H₂SO₄ extraction.

1436. SNAPIR, JOACHIM (assigned to Zinnwerke Wilhelmshurg G. m. b. H.). German Patent 678,951, July 26, 1939; *Chem. Abs.*, vol. 33, 1939, p. 9562^e.

In purifying Zn plating solution, Ni is removed by addition of dimethylglyoxime to the neutral solution, digesting for some hours at 60°-70° C., and filtering. The Ni is recovered by treating the residue with H₂SO₄, and filtering the dissolved Ni from the regenerated dimethylglyoxime.

IN MANGANESE METALLURGY

1437. AGLADZE, R. I. [Hydrometallurgical Production of Metallic Manganese.] *Tekhnika*, Nos. 7, 8, and 9, 1939, pp. 95-102 (in Georgian); *Khim. Referat. Zhur.*, No. 8, 1940, p. 81 (*see Chem. Abs.*, vol. 36, 1942, p. 2209^b); *Chem. Abs.*, vol. 36, 1942, p. 6087^a.

Precipitation of Ni and Co, as well as possible impurities of Zn and Cu, from the electrolyte solution is carried out by addition of Na₂S. Complete precipitation of Ni and Co requires a small excess of Na₂S. Ni and Co can be precipitated also by adding electrolytic Mn powder, which decomposes H₂O and increases the pH value. Precipitated Mn (OH)₂ retards the precipitation of Ni and Co. The methods proposed for producing metallic Mn and MnO₂ from ores consider the recovery of H₂SO₄ formed during the electrolysis of MnSO₄. This H₂SO₄ can be used to leach new quantities of Mn from the ores. The leaching of manganese carbonate ores can be carried out with spent electrolyte. Manganese hydrometallurgy includes the recovery of Ni, Co, and other nonferrous and noble metals.

1438. BASORE, C. A., AND EILAND, E. M. Utilization of Low-Grade Alabama Manganese Ores. *Bull. Alabama Polytech. Inst. Eng. Exper. Sta. Bull.* 7, 1936, 16 pp., *Chem. Abs.*, vol. 31, 1937, p. 2140¹.

Two types of Mn ores are amenable to leaching treatment—(1) soft and (2) hard. Soft ores in lumps of any size can be leached in 5 minutes with a 1-percent SO_2 solution at room temperature. The Mn from the hard ores was best extracted by crushing the ores to 200-mesh, extracting with 200 percent excess 1 percent SO_2 in water at 45°C . for 5 minutes. Under these conditions, 71–96 percent of the Mn content was extracted. The ores contained 5.4–43.5 percent Mn; Fe, Co, SiO_2 , and P are present as impurities. The Co can be extracted as a byproduct. The SO_2 extracts were treated with fresh ore, and the Fe and P were rendered insoluble and filtered off. The filtrate, upon evaporation to solid MnSO_4 , and calcination, yielded MnO_2 , containing only 0.02–0.008 percent of Fe and a trace of P. Approximately half the excess SO_2 was not recoverable for reuse.

1439. BOGOMOLOV, Y. A. [Rare Metals in the Smelting of Iron.] *Teoriya Prakt. Met.*, vol. 9, No. 2, 1937, pp. 84–88; *Chem. Zentralbl.*, vol. I, 1938, p. 408; *Chem. Abs.*, vol. 33, 1939, p. 6763⁴.

A review of the possibility of extracting the following metals occurring in Mn and Fe ores: Cd, Se, Te, Ga, Tl, In, Ge, Re, Co, Sc, Hf, Rb, and Cs is presented.

1440. ELECTROMANGANESE CORP. Electrolytic Purification in Manganese Electrowinning. British Patent 627,208, Aug. 3, 1949 (*see Chem. Abs.*, vol. 42, 1948, p. 7171g); *Chem. Abs.* vol. 44, 1950, p. 1836a.

In Mn electrowinning, the electrolyte must remain low in Mo. The upper critical maximum concentration is 0.0015 gm. per l. of solution. The spent electrolyte is oxidized with cell sludge, additional Mn ore is added and after digesting, the pH is adjusted to 5.5–6.0, which precipitates Fe and some of the Mo as sludge. The pH is then adjusted to 7.0–7.5 and $(\text{NH}_4)_2\text{S}$ added to precipitate the Mo, Co, and Ni.

1441. FRASER, COLIN, AND OTHERS. Brief Description of the Risdon Works of the Electrolytic Zinc Co. of Australia, Ltd. *Proc. Australasian Inst. Min. Met.*, No. 95, 1934, pp. 247–291; *Chem. Abs.*, vol. 29, 1935, p. 4677².

In a complicated flowsheet involving hydrometallurgical, pyrometallurgical operations and electrolysis, Co is recovered as a byproduct from a Zn plant, with by-products of Ag, Cd, and others.

1442. NIKOLADZE, R. [The Significance of the Chiaturian Manganese Deposits As a Source of Rare Metals.] *Tekhnika*, Nos. 7, 8, and 9, 1939, pp. 103–112 (in Georgian); *Khim. Referat. Zhur.*, No. 8, 1940, pp. 19–20; *Chem. Abs.*, vol. 36, 1942, p. 6451².

Data on the effects of alloying elements (C, Si, Mn, Cu, Al, Ni, Cr, W, Mo, and V) on the properties and cost of special steels, and analyses of various grades of Chiaturian Mn ores are given. The ores contain a number of valuable metals, especially Ni and Co. In their composition these ores represent a natural mixture for electric furnace production of ferromanganese or silicomanganese. These Mn ores can also be used as a source of Ni, Co, Ti and V.

1443. SCHATZ, R. W. Electrolytic Manganese Metal From the Ores of the Olympic Peninsula, Washington. *Washington State Coll. Min. Exper. Sta. Bull.* W, 1939, 27 pp; *Chem. Abs.*, vol. 34, 1940, p. 5390⁴.

Of 23 ores examined from this area for leachability 10 were combined into a composite analyzing Mn 27.2 percent, Fe 10.4 percent, and extraction tests were made. The removal of Fe, Cu, As, Co, and Ni impurities from the leached Mn solution is discussed. The suggestion is offered that the addition of powdered Mn might precipitate and remove Cu, Co, and Ni. A flowsheet almost identical with that of electrolytic Zn is suggested. Extraction of at least 95 percent of the Mn can be expected by use of a reducing roast and a dilute H_2SO_4 leaching process before electrolysis.

1444. SCHLAIN, DAVID, JACOBS, J. H., SHELTON, F. K., AND KNICKERBOCKER, R. G. Recovery of Cobalt From Manganese Ores in Production of Electrolytic Manganese. (A) Cobalt Content of Manganese Ores. (B) Separation and Electrodeposition of Manganese and Cobalt From Manganese Electrolytes. Bureau of Mines Rept. of Investigations 3866, pp. 1–12 and 13–18; *British Abs.*, 1946, p. B–I–304; *Chem. Abs.*, vol. 40, 1946, p. 5678⁴.

The Co and Mn contents of a large number of United States and a few foreign Mn deposits are listed. The deposits in the southeast part of the United States contain the most Co (0.1–several percent). Co is easily removed from Mn leach solutions by precipitation, with other impurities by means of H_2S in the usual manner. The purified solution is suitable for feeding to Mn deposition cells. Mn is dissolved from the mixed precipitated sulfides by treatment with dilute H_2SO_4 , and after calcination the remaining sludge is extracted with boiling dilute H_2SO_4 to recover the Co. After the solution is purified, Co is precipitated as carbonate by Na_2CO_3 and may be obtained as oxide or metal by roasting, reduction, or electrolysis.

1445. SHELTON, S. M. Electrodeposition of Manganese. U. S. Patent 2,169,540, Aug. 15, 1939 (*see Chem. Abs.* vol. 32, 1938, p. 6162²); *Chem. Abs.*, vol. 33, 1939, p. 9157⁷.

In the electrodeposition of metallic Mn from an aqueous sulfate solution, a xanthate such as sodium-ethyl xanthate or amyl xanthate is preliminarily added to remove Ni and Co.

IN MISCELLANEOUS PROCESSES

1446. BANERJEE, N. G., AND BANERJEE, T. Recovery of Nickel and Zinc From Silver Refinery Waste Liquors. Part I. Recovery of Nickel by Electrodeposition. *Jour. Sci. and Ind. Res. (New Delhi, India)*, vol. 11B, February 1952, pp. 76–78; *Metals Rev.*, vol. 25, No. 5, May 1952, p. 18 (166–A).

Tables and graphs are given.

1447. BEALL, J. V. Carteret Copper Refinery. *Min. and Met.*, vol. 29, 1948, pp. 658–659; *Chem. Abs.*, vol. 46, 1952, p. 2976d.

Describes a Cu extracting and refining operation, in which the Cu is also electrolytically refined. The electrolyte is concentrated enough to precipitate nickel sulfate, which is removed and shipped for refining.

1448. BENARD, FREDERIC. Anode-Furnace Refining of High-Nickel Blister Copper. *AIIME Tech. Pub.* 910, 1938, 5 pp.; *Chem. Abs.*, vol. 32, 1938, p. 2433².

The blister Cu under investigation contains 0.50–1.5 percent of Ni. Only a portion of the Ni is removed during furnace treatment preliminary to casting the anodes; of the amount present in the cast anodes, a varying percentage is found in anode slime. Roasting and leaching of the slimes must be repeated several times before Ni is low enough to send slimes to the doré furnace. This increases treatment charges, Se losses, and tieup of values. In furnace refining, a NiO compound is formed that is soluble in Cu and does not slag off. By forming low-O anodes, Ni in slimes was greatly reduced. For example, the following results were obtained by blowing air on the launder stream and poling to a high crown set respectively: Ni in anode 0.71, 0.61; O in anode 0.23, 0.06; Ni in slimes 30.0, 2.6 percent; total Ni in slimes 22.0, 2.6 percent.

1449. BETTERTON, J. O., AND LEBEDEF, Y. E. (assigned to American Smelting & Refining Co.). Removal of Ni From Substantially Nonferrous Pb-Bearing Metals Which May Contain 4 or 5 Percent of Ni.

U. S. Patent 2,329,817, Sept. 21, 1944; Chem. Abs., vol. 38, 1944, p. 946³.

A process, if employed for removal of Ni from predominantly nonferrous Pb-bearing metals, such as an impure "white metal," which involves treating a molten bath of the metal with Si in the presence of an inert cover of material, such as a sodium silicate, having a specific gravity less than that of the Si so that the Si passes through it in contact with the metal bath; and removing nickel silicide from the metal bath as a floating crust (the bath used being substantially free from oxygen and S compounds, reactive with Si).

1450. CROCKETT, R. E. (assigned to H. A. Brassert & Co.) Recovery of Asbestos. U. S. Patent 2,500,154, Mar. 14, 1950; Chem. Abs., vol. 44, 1950, p. 5040b.

An economically feasible method for recovering asbestos fibers from the tailings of the chrysotile mining operations is described. In separating crushed chrysotile from accompanying serpentine rock, substantial quantities of asbestos fibers are discarded with the latter. These fibers can be detached from the other components by subjecting a slurry of the ground tailings to violent agitation and scrubbing, removing Fe, Ni, and Cr ore by means of a wet magnetic separator, and then tabling the coarse tailing and middling products from the magnetic separator. A Cr concentrate, a serpentine middling product, and an asbestos tailing are produced. The asbestos tailings are classified further by tabling and screening; the fibers thus recovered are of commercially valuable length and high quality. The production cost of the fiber is reduced by simultaneous recovery of Cr, Ni, and Fe ore.

1451. DESCHACHT, —. [The Copper of Katanga.] *Cuivre et laiton*, vol. 12, 1939, pp. 33–41; Chem. Abs., vol. 33, 1939, p. 2858⁴.

Discusses geographical and geological conditions in the last 25 years of development of Cu production and byproducts of Co, Sn, Zn, Ag, Au, Ra, Pd, and Pt.

1452. DUTTA, R. K., AND BANERJEE, T. (National Metallurgical Laboratory, Jamshedpur). Recovery of Nickel and Zinc From Silver Refinery Waste Liquor. II. Chemical Methods. *Jour. Sci. Ind. Res. (India)*, vol. 11B, 1952, pp. 342–343 (*see* Chem. Abs., vol. 47, 1953, p. 11,043h); Chem. Abs., vol. 48, 1954, p. 1911d.

Si refinery-waste effluent containing about 0.45 percent each of Ni and Zn is added, with vigorous stirring, to a solution containing NaOH and NaClO. The precipitate is separated, washed with NaOH and water, dried, and ignited at 500° C. The product contains 95.5 percent of Ni and 4.5 percent of Zn.

1453. HIRSH, KUPFER- UND MESSING-WERKE, A. G. [Nickel.] German Patent 583,545, Sept. 5, 1933; Chem. Abs., vol. 28, 1934, p. 979⁴.

Electrolytic Ni is prepared from Ni-H₂SO₄ residues obtained as a byproduct in the Cu electrolysis processes by neutralizing the excess of H₂SO₄ through addition of Ca(OH)₂ or other substances forming insoluble sulfates, removing the precipitated sulfate, concentrating the NiSO₄ solution and electrolyzing this.

1454. HORALEK, K. [Cobalt From Roasted Pyrites.] *Angew. Chem.*, vol. 63, No. 21, 1951, pp. 525–527; *Metals Rev.*, vol. 25, No. 3, March 1952 (82-B).

The procedure of extracting Co from Fe ore is discussed. The data, charted and tabulated, show that Co production varies greatly with time and country and that the Co content of Fe ores varies greatly with the source. (10 refs.)

1455. HUNYADY, ISTVAN. Treating Aluminum or Copper Ores. British Patent 456,500, Nov. 10, 1936; Chem. Abs., vol. 31, 1937, p. 2158⁵.

Ni and Co are obtained as byproducts. In a treatment with ammonium sulfate, acidulated water, oxidiz-

ing air, ammonium alum is obtained, and upon reduction ferrous ammonium sulfate is crystallized out. The remaining metals, including Ni and Co, are precipitated by addition of ammonia, and separated into groups by successive treatments with carbonated water, with further NH₃ to remove Ni, Co, and others, and with (NH₄)₂CO₃. The NH₃ extract containing Cu, Ni, Co, Cr, and V is boiled to precipitate Cu, Ni, and Co; Cu is then removed as sulfide.

1456. ISHIZUKA, HIROSHI. [Refining of Iron Oxides and Iron.] Japanese Patent 5553, Sept. 21, 1951; Chem. Abs., vol. 47, 1953, p. 3211b.

Iron oxides, including Fe sand, containing ferric oxide are mixed with metallic Fe in slight excess of the amount needed to form ferrous oxide by fusion. The purified ferrous oxide on top is separated from the lower layer containing Cu, Ni, As, and metals nobler than Fe.

1457. KAMECKI, J. AND SEDZIMIR, J. [Obtaining Cobalt as a Byproduct During the Hydrometallurgical Treatment of Lean Polymetallic Ores.] *Hutník*, vol. 21, No. 10, October 1954, pp. 321–324; *Metals Rev.*, vol. 28, No. 3, March 1955, p. 24 (48-B); Chem. Abs., vol. 49, 1955, p. 2965e.

Discusses method recovering Co from Cu pyrite ores.

1458. LASSENIUS, T. Byproducts of the Cellulose Industry. Finnish Paper Timber Jour., vol. 26, 1944, pp. 73 and 85. *Tech. Bull. Paper Maker's Assoc. (Great Britain and Ireland)*, vol. 21, p. 45; Chem. Abs., vol. 39, 1945, p. 617¹.

Various byproducts from the cellulose and the sulfate mills are discussed, with possible uses. The pyrites ash (200,000 tons) is used for manufacturing Fe and as a source of Co.

1459. LUTJEN, G. P. Cobalt Camp Comes Back. *Eng. and Min. Jour.*, vol. 151, No. 11, November 1950, pp. 86–91; *Eng. Index*, 1951, p. 225.

High-grade Si ore and values in Co indicate why famous old camp at Cobalt, Ontario, is being revived. Silver Miller's 140,000 oz. output monthly comes half from mill (formerly substation), and half from rich veins, hand-picked and sent direct to smelter. Several other companies are active in prospecting, mining, and ore treatment.

1460. PERVUSHIN, S. A. [The Cobalt Problem in the U. S. S. R.] *Redkie Metal*, vol. 4, No. 3, 1935, pp. 6–13; Chem. Abs., vol. 30, 1936, p. 2889².

Complex ores containing small amounts of Co are found in large quantities. These can be commercially treated, with Co as byproduct.

1461. SANTOS, T. D. S. (University of São Paulo, Brazil). [General Principles of Pyrometallurgical Processes for Refining of Tin.] *ABM (Bol. assoc. brasil metais, São Paulo)*, vol. 9, 1953, pp. 199–218; Chem. Abs., vol. 48, 1954, p. 4399a.

Review of processes that remove Cu, As, Sb, Fe, and Ni by adding Al; Pb, Cu, and Ni by adding S; and Fe by adding Si. The removal of impurities by the addition of alkalis or alkaline earth metals to crude Sn may be possible (16 refs.).

1462. STADLINGER, HERMAN (Köthen, Anhalt, Germany). [Mansfeld Copper Ores.] *Chem. Ztg.*, vol. 74, 1950, pp. 722–725; Chem. Abs., vol. 45, 1951, p. 5577i.

The Cu-Ag ores of Mansfeld, Thuringia, are the most important deposits of this kind in Germany and famous for over 750 years. They occur in marine sediments of the lower horizons of the Upper Permian (Zechstein), which are bituminous marls and slates. Especially beds of Sangerhausen containing 2–5 percent of Cu promise in the future a satisfactory Cu production. Ag, Zn, Pb, and Ni are byproducts of the Cu

metallurgy. The genesis of the ores is discussed, including the role of bacteria and theories of epigenetic and syngenetic formation.

- 1463.** TOPUNOVA, G. A. [Sulfide-Magnetite Ores as a Basis of the Cobalt Industry in Russia.] *Tsvetnyye Metal*, Nos. 5-6, 1940, pp. 35-36; *Chem. Abs.*, vol. 35, 1941, p. 6219¹.

Exploratory work in 1938-39 showed that certain Ural deposits of magnetite with embedded sulfides are a potential source of Co, which exists in the sulfides in an isomorphous admixture. The magnetite ores are used for the blast furnaces of the Tagil steel works and are previously purified from S by magnetic separation. Topunova suggests that methods be worked out for enriching sulfide tailings to produce Co concentrate.

- 1464.** UCHINO, MASAO. [Recovery of Cobalt as Byproduct in Hydrometallurgy of Certain Iron Sulfide Ores Containing Copper.] *Repts. Imp. Ind. Research Lab., Osaka, Japan*, vol. 10, No. 16, 1930; *Chem. Abs.*, vol. 24, 1930, p. 2970¹.

A comprehensive study of recovery (or separation) of Co from other elements, especially Cu.

- 1465.** WHITAKER, M. E. Recovery of Byproduct Metals in Smelting of Copper-Alloy Scrap. *Metallurgia*, vol. 40, No. 240, October 1949, pp. 295-304; *Eng. Index*, 1950, p. 256.

Methods are surveyed whereby Zn, Sn, Pb, Ni, and Cd can be recovered as byproducts in smelting low-grade Cu alloy scrap and residues, instead of being lost in flue dust and slags. Discussed also are methods of collecting and segregating scrap, methods of recovering flue dusts and winning of Zn, Sn, Pb, and Cd from them and recovery of Ni.

RECOVERY FROM SCRAP SOURCES SPENT CATALYSTS

- 1466.** BELEKAR, G. K., KANE, J. G., AND SHAHANI, H. S. (University of Bombay). Utilization of Byproducts and Waste Products of the Fatty-Oil Industry. I. Recovery of Nickel From Spent Nickel Catalysts. *Jour. Sci. Ind. Res. (India)*, vol. 11B, 1952, pp. 28-30; *Chem. Abs.*, vol. 46, 1952, p. 6852c; *Metals Rev.*, vol. 25, No. 4, Apr. 1952, p. 17 (121-A).

Five spent catalyst samples were digested with 10-50 percent of H_2SO_4 and with various H_2SO_4 - HNO_3 mixtures of 15- to 70-percent, and 20- to 70-percent proportions. Higher recoveries of Ni (93.2-98.3 percent) in the combined mother liquor and washings were obtained by mixed acid treatment (27 refs.).

- 1467.** BHASIN, M. M., GUPTA, J., AND AGGERWAL, J. S. (National Chemical Laboratory, Poona, India). Recovery of Nickel and Fat From Spent Nickel Catalyst. *Jour. Sci. Ind. Res., India*, vol. 11B, 1952, pp. 248-249; *Chem. Abs.*, vol. 47, 1953, p. 5044i.

The material is acted upon with dilute HCl, followed by extraction with petroleum ether. The aqueous fraction is treated with precipitated chalk or ammonia to precipitate Fe. The Ni is then precipitated as carbonate and used as such or can be converted to the formate.

- 1468.** BIJAWAT, H. C., AND BEDEKAR, S. G. Recovery of Nickel and Fat From Spent Hydrogenation Catalysts. *Jour. Sci. Ind. Res., India*, vol. 13B, 1954, pp. 572-575 (*see Chem. Abs.*, vol. 47, 1953, p. 5044i); *Chem. Abs.*, vol. 49, 1955, p. 6507i.

Optimum conditions for large-scale recovery of Ni and fat from commercial spent hydrogenation catalysts are reported, and the economics of the process is

evaluated. A method is described for removing Fe from the spent catalyst. The material is digested with 5 percent H_2SO_4 to solubilize Ni, and enough Na_2CO_3 is added to precipitate Fe when air is blown through for oxidation. After the Fe is separated, more Na_2CO_3 is introduced to precipitate $NiCO_3$ on boiling, which is then treated with H_2SO_4 to produce $NiSO_4$, a salt suitable for use as catalyst.

- 1469.** BOLDINGH, JAN (Lever Bros. & Unilever, N. V.). [Separation of Constituents of Fatty Oils and Their Derivatives by Dialysis.] *Netherland Patent* 72,285, May 15, 1953; *Chem. Abs.*, vol. 48, 1954, p. 1033f.

Components of fatty oils or their derivatives are separated by dialysis, preferably in the presence of a solvent, through a rubber membrane that swells in contact with oil. The dialysis of polar substances is accelerated by the use of polar rubbers and nonpolar solvents. Among examples cited is elimination of Ni catalyst from extracted fat obtained in the hardening of fatty oils.

- 1470.** ETINBURG, E. Y., AND POPOV, M. S. Novoe v Praktike Hidrogenizatsii Zhirov, Vsesoyuz. [A Comparative Evaluation of Methods for Purifying Nickel Sulfate Solutions.] *Nauch.-Issledovatel. Inst. Zhirov.*, 1939, pp. 74-81; *Khim. Referat. Zhur.*, 1940, No. 3, p. 120; *Chem. Abs.*, vol. 36, 1942, p. 3013².

Various methods for purifying $NiSO_4$ solution obtained by boiling Ni catalyst with H_2SO_4 were investigated. Oxidation with NaClO has the advantages over air oxidation of more complete removal of Fe; it requires a smaller excess of Na_2CO_3 .

- 1471.** HEUBLYUM, R. [Recovery of Nickel From Kieselguhr Catalysts.] *Seifensieder Ztg.*, vol. 60, 1933, pp. 599-600 and 628-629; *Chem. Abs.*, vol. 27, 1933, p. 5999.

The oil in the catalyst is extracted and the residue dissolved in H_2SO_4 . To free the Ni solution from Fe, neutralize with Na_2CO_3 at 50°-60° C., and determine the amount of Fe in solution.

- 1472.** HOUGHTON, A. S. (assigned to Allied Chem. & Dye Corp.). Production of Metallic Catalysts. U. S. Patent 2,289,784, July 14, 1942; *British Abs.*, 1943, p. B-I-382.

A mass of metal (Ni, Cu, or Co), for example, spent hydrogenation catalyst, is treated (at room temperature to the boiling point) with a solution of oxalic (0.1-1.5 N), malic or tartaric acid, or their salts, and an oxidizing agent (0.1-4.0 N HNO_3) to promote attack on the metal and to favor the formation of a layer of the corresponding metal salt, which is subsequently decomposed—for example, by heating to 300°-380° C. in an oxidizing atmosphere to form a fresh catalytic surface. Alternatively, the metal surface may be preoxidized and then treated with the solution of acid.

- 1473.** IMPERIAL CHEMICAL INDUSTRIES, LTD. [Regenerating Nickel Catalysts.] *French Patent* 853,753, Mar. 28, 1940; *Chem. Abs.*, vol. 36, 1942, p. 2694⁶.

A Ni catalyst used conjointly with an inert support for the manufacturing polyhydric alcohols can be regenerated by dissolving the Ni by means of an acid and treating the resulting acid solution containing the Ni and the support with an excess of alkali to precipitate nickel hydroxide. The solid matter is separated from the solution, washed, and dried; the dried product is treated at high temperature with H_2 to reduce the nickel hydroxide to metallic Ni.

- 1474.** IPATIEFF, V. N., AND CORSON, B. B. (assigned to Universal Oil Products Co.). Regenerating Spent Reduced Nickel Catalysts Such as Those Used for Hydrocarbon Oil Conversion. U. S. Patent 2,267,736, Dec. 30, 1942 (*see Chem. Abs.*, vol. 35, 1941, p. 2708³); *Chem. Abs.*, vol. 36, 1942, p. 3038².

Spent, reduced Ni catalysts containing S compounds of Ni are heated with chlorine at about 550°–900° F. to convert the S compounds to chloride; the chloride is then reduced to metal by heating with NH_3 at about 550°–900° F.

1475. ISHIBASHI, SATURO. [The Recovery of Nickel Oxide and Molybdenum Oxide From the Waste Catalyst. I. Recovery of Nickel Oxide.] Jour. Electrochem. Soc., Japan, vol. 19, 1951, pp. 185–189; Chem. Abs., vol. 46, 1952, p. 1725b.

The roasted powder of the waste mixed catalyst composed of NiO , MoO_3 , and clay used for hydrocracking petroleum was treated first with 40 percent HNO_3 at 80° C. By adding $\text{Fe}(\text{NO}_3)_3$ at pH 4.0 to 4.2, a small quantity of molybdic acid, which was dissolved in this $\text{Ni}(\text{NO}_3)_2$ solution, was removed as insoluble ferric molybdate. The purified $\text{Ni}(\text{NO}_3)_2$ solution was converted to ammonium nickel nitrate complex salt solution by adding an excess of NH_4OH . The solution was diluted to a concentration of about 0.2 percent $\text{Ni}(\text{NO}_3)_2$ with water and then boiled; over 98 percent of the Ni was obtained as a nongelatinous precipitate. By these operations, about 92 percent of NiO in the waste catalyst was recovered, including only 0.05 percent of $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$, 0.03 percent of MoO_3 , and a trace of SO_2 .

1476. KAZAKOVA, L. [Recovery of Nickel Catalyst With Sulfuric Acid, With the Addition of Sulfonic Acids.] Masloboino Zhirovoe Delo, vol. 12, 1936, pp. 145–146; Chem. Abs., vol. 30, 1936, p. 5371⁺.

In the recovery of spent nickel formate catalyst with the aid of sulfonic acids, a good emulsification of fat and rapid dissolution of Ni in H_2SO_4 and separation of oil (2–5 minutes in laboratory) are effected. A mixture of 15 percent excess of H_2SO_4 , 20° B., 3 percent sulfonic acid and 100 gm. of catalyst (containing 11 percent of Ni) was heated on a water bath with stirring, giving a solution with 10.2 gm. of Ni.

1477. KIMURA, GORO (assigned to Hokkai Yushi Kogyo K. K.). [Recovery of Waste Nickel Catalyst.] Japanese Patent 99,594, Feb. 16, 1933; Chem. Abs., vol. 28, 1934, p. 2559⁺.

Waste Ni catalyst used for hardening oils is dissolved in H_2SO_4 containing HNO_3 . To the solution, NaOH or Na_2CO_3 is added in such amount that Ni is not precipitated, but most of the Fe and other impurities are precipitated. After separation from the precipitate, the solution is heated with a small amount of an oxidizing agent (such as KMnO_4 or Na_2O_2), by which the remaining Fe is precipitated. Ni is recovered as hydroxide with caustic alkali from the filtrate.

1478. KLEIN, OTTO, AND MEYER, KARL (assigned to Braunkohle Benzol, A. G.). [Reclaiming Cobalt and Thorium From Spent Contact Catalysts.] German Patent 722,553, May 28, 1953 (*Cl. 120 1.03*); Chem. Abs., vol. 37, 1943, p. 5205⁺.

After the catalyst is dissolved in H_2SO_4 and the residue removed, Th is precipitated as the double sulfate with potassium sulfate and filtered, Fe is removed as hydrated oxide from alkali carbonate precipitation, and finally cobalt carbonate is precipitated.

1479. KO, KYORII. [Recovery of Waste Nickel and Hydrolysis of Fats and Oils.] Japanese Patent 91,233, Apr. 28, 1931; Chem. Abs., vol. 26, 1932, p. 1466.

Fats or oils to be hydrogenated are heated at 130° C., mixed with Ni catalyst, and treated with H_2 . When the hydrogenation is completed, the temperature of the substance is kept at 170°–220° C., a milky solution of Twitchell reagent and H_2SO_4 are added under agitation, and then the whole is treated with steam. Over 95 percent of the oil is hydrolyzed. The oily layer floats and

a mixture of glycerol and NiSO_4 solution forms the outer layer. NiSO_4 is changed into $\text{Ni}(\text{OH})_2$, and then NiCO_3 .

1480. KOONTZ, J. D. (assigned to Standard Oil Development Co.). Recovery of Cobalt Catalyst After Reaction of Carbon Monoxide and Hydrogen With Olefins. U. S. Patent 2,679,534, May 25, 1954; Chem. Abs., vol. 48, 1954, p. 10, 3291.

In the carbonylation process in which carbon compounds containing olefinic double bonds react with CO and H_2 under pressure in the presence of a Co catalyst, the catalyst is recovered from the crude aldehyde product in the form of a metal, a formate, or a basic formate. In the recovery of the catalyst under pressure in a pressure vessel at 250°–500° F., enough pressure is maintained to allow at least 5 percent of the water to be present in the liquid phase. After the treatment the mixture is cooled and centrifuged. The centrifuge product contains only 4–8 p. p. m. Co as contrasted with 100–500 p.p.m. in the conventional treatments.

1481. KOPEIKOVSKII, V., AND LAPINA, T. [Recovery of Copper and Nickel From the Spent Catalyst in the Hydrogenation of Oils.] Masloboino Zhirovoe Delo, vol. 12, 1936, pp. 580–581; Chem. Abs., vol. 31, 1937, p. 5194⁺.

In the hydrogenation of oils by Vasilév's method (see Chem. Abs., vol. 30, 1936, p. 889⁺) with Cu-Ni catalyst without a carrier, separation of the contact mixture from fat mixture by filtration is impossible. A recovery of 67 percent of Ni and 55 percent of Cu was effected by settling the fat mixture in special boxes and heating the settled portion with 9 percent of commercial H_2SO_4 with live steam for 1 hr. The top layer of pure fat mixture is removed, and the lower and intermediate layers are treated with Na_2CO_3 . The hydroxides of Ni and Cu are filtered off and reworked into catalysts as usual.

1482. MATSUMARU, HIDEO, AND UYA, KIYOO (assigned to Takeda Drug Industries Co.). [Regeneration of Waste Nickel Catalyst.] Japanese Patent 175,781, Mar. 11, 1948; Chem. Abs., vol. 44, 1950, p. 8566h.

The HNO_3 extraction of waste Ni catalyst is treated with NH_4OH in excess to precipitate the Fe, and the filtrate containing a complex salt of Ni is concentrated in vacuo, kept at 47° C. under CO_2 for 30 min., and then reduced to Ni metal.

1483. MATUMOTO, TUNETARŌ. [Separation of Pure Nickel From Waste Catalyst.] Tokyohuritu Kogyo-syoreikwan Kwagaku Kenkyu (Repts. Chem. Research, Prefectural Inst. Advancement Ind. Tokyo), No. 3, 1940, pp. 19–22; Chem. Abs., vol. 35, 1941, p. 7664⁺.

When waste Ni catalyst solution is made to pH 8.3 or more by the addition of alkali, all Ni and ferrous salts are precipitated. Ferrous Fe is oxidized to Fe^{+++} by air bubbles. Then H_2SO_4 is added to pH 2.7–4.3, and the mixture is heated. Nickel is dissolved as NiSO_4 , and $\text{Fe}(\text{OH})_3$ remains undissolved. This method can be applied also to the waste catalyst containing some Cu.

1484. RANEY, MURRAY. Method of Reclaiming Catalytic Material From Spent Catalytic Material. U. S. Patent 2,139,602, Dec. 6, 1938; British Abs., 1943, p. B-1-382; Chem. Abs., vol. 33, 1939, p. 2099⁺.

Spent Ni catalyst contaminated with oil and siliceous support is roasted to oxidize the metal and then mixed with flux (for example, borax glass) and a reducing metal (Al) in sufficient amount to reduce the oxide and form an alloy (for example, a 50–50 Ni–Al alloy). The mixture is ignited by, for example, a Mg fuse, cooled, and the slag separated from the metal, which is extracted with NaOH to regenerate the Ni catalyst.

1485. ROELEN, OTTO, AND HAINISCH, FRANZ (assigned to Hydrocarbons Synthesis Corp.). Cobalt Recovery From Spent Catalysts. U. S. Patent 2,215,885, Sept. 24, 1941; Chem. Abs., vol. 35, 1941, p. 861².

A method of recovering Co values from catalysts prepared by precipitating compounds of Co onto kieselguhr, which have been used in the synthetic production of benzine from CO and H₂, by which a paraffinic deposit has been formed on the catalysts, involves treating the catalyst with a solution containing HNO₃ until the Co is dissolved, the solution containing throughout the process a concentration of about 3-5 percent of HNO₃, and separating the resulting solution from the kieselguhr.

1486. SHCHERBAKOV, N. [Separation of Nickel Catalyst From Fat Mixtures.] Masloboino Zhirovoe Delo, vol. 12, 1936, pp. 208-209; Chem. Abs., vol. 30, 1936, p. 5437⁵.

1487. SHLIFER, D. [New Way of Converting Recovered Nickel Carbonate Into Sulfate in the Hydrogenation of Fats.] Masloboino Zhirovoe Delo, vol. 15, No. 6, 1939, p. 15; Chem. Abs., vol. 34, 1940, p. 3522⁵.

In the recovery of Ni catalyst by precipitation with CaCO₃ and dissolution of an aqueous suspension of the NiCO₃ in H₂SO₄, the use of steam can be eliminated by treating the moist NiCO₃ filter cake with concentrated H₂SO₄. The exothermic reaction is completed at 70°-90° C. without additional heating.

1488. SMITH, W. M., LUENING, W. D., AND LANE, S. C. (assigned to Standard Oil Development Co.). Removal of Cobalt From Olefin, Carbon Monoxide, Hydrogen Reaction Mixtures. U. S. Patent 2,596,920, May 13, 1952; Chem. Abs., vol. 47, 1953, p. 1728f.

An aldehyde-rich mixture produced by the cobalt-carbonyl-catalyzed reaction of olefins with CO and H₂ is freed of Co by the thermal decomposition of the catalyst, but under conditions lessening destruction of the desired aldehydes. Thus, heating such mixtures rapidly at 100 p. s. i. to 310° F. reduces the percentage of Co from 0.18 to 0.001.

1489. STANDARD OIL DEVELOPMENT CO. Carbonylation Catalyst. British Patent 691,006, May 6, 1953; Chem. Abs., vol. 48, 1954, p. 8249a.

In the synthesis of oxygenated compounds (notably alcohols) from organic compounds containing at least one nonaromatic C-C double bond and a mixture of Co and H₂, the Co catalyst, when recovered, can be reused without first being converted into an organic salt. The catalyst is ground in a liquid organic medium, such as alcohol distillation bottom, and is then made into a paste or gel by adding a neutral, organic, paste-forming substance, for example, petrolatum, paraffin wax, or Co soap concentrate, such that the composite contains about 50 percent (by weight) of Co.

1490. STERLIN, B. [Recovery of Nickel From Spent Catalyst by Preliminary Treatment With Dichloroethane.] Masloboino Zhirovoe Delo, vol. 16, No. 4, 1940, pp. 13-16; Chem. Abs., vol. 35, 1941, p. 921⁷.

The procedure consists substantially in 2 alternate treatments of the spent catalyst with 1.5 parts by weight of pure C₂H₅Cl₂ at 70° C. for about 0.5 hr., filtration on a filter press, and removal of the entrained solvent by injection of steam. The filtered residue (40-42 kg.) is stirred with 250 l. H₂O, and after the addition of 110-140 kg. of concentrated H₂SO₄, is heated directly with steam until dissolved. The excess H₂SO₄ is neutralized with Na₂CO₃ and filtered, and the NiSO₄ in the filtrate is used in the preparation of catalyst as usual.

1491. TAYLOR, A. W. C., AND ACKROYD, NORVIK (assigned to Imperial Chemical Industries, Ltd.). Separation of Aldehydes and Olefins From Cobalt. Brit-

ish Patent 655,976, Aug. 8, 1951; Chem. Abs., vol. 46, 1952, p. 7581a; U. S. Patent 2,609,337, Sept. 2, 1952; Chem. Abs., vol. 47, 1953, p. 146e.

Aldehydes obtained by reaction of olefins and CO with Co as a catalyst and unreacted olefin are separated from Co by flash distillation.

1492. TSIVINA, P. A., AND GIRMAN. [Regeneration of Used Catalysts.] Novoe v Praktike Hidrogenizatsii Zhirov, Sbornik Vsesoyuz; Nauch-Issledovatel. Inst. Zhirov (Leningrad), 1939, pp. 95-97; Khim. Referat. Zhur., No. 4, 1940, p. 109; Chem. Abs., vol. 36, 1942, p. 3916⁹.

Experiments were carried out to improve regeneration of the Cu-Ni catalyst for a maximum extraction of Cu and Ni. Treat the catalyst with hot water, mix with live steam at 90° C., add 2 percent of NaOH and 4 percent of kieselguhr, oxidize for 60 minutes with a solution containing 30-40 gm. per l. of active chlorine, and boil at 100° C., with an excess of 15-20 percent H₂SO₄. This gives satisfactory results under plant conditions.

1493. VENO, SEIICHI, MATSUDA, NUBUO, AND OGAMI, HAJIME. [Recovery of Nickel Catalyst Used for Hydrogenation of Oil.] Jour. Nippon Oil Technol. Soc., vol. 2, No. 5, 1949, pp. 1-10; Chem. Abs., vol. 44, 1950, p. 5497i.

General methods of recovery.

1494. WELLS, B. D. (assigned to Universal Oil Products Co.). Regenerating Spent Metal Catalysts Such as Nickel Used for Treating Petroleum Oils Containing Sulfur. U. S. Patent reissue 22,097, May 12, 1942; reissue of original Patent 2,225,811 (Chem. Abs., vol. 35, 1941, p. 2708⁹); Chem. Abs., vol. 36, 1942, p. 7295⁹.

1495. YAKUBOV, M. [Separation of the Catalyst From Fat Mixture by Centrifuging.] Masloboino Zhirovoe Delo, vol. 14, No. 6, 1938, pp. 16-18; Chem. Abs., vol. 33, 1939, p. 5687⁹.

Several advantages are claimed for precipitating the Cu-Ni catalyst from the fat mixture by the method of centrifuging, which is described.

1496. YAMAMOTO, KAZUMI, AND SATO, KAZUTOSHI (assigned to Mitsui Chemical Industries Co.). [Recovery of Waste Catalyst From the Carbonyl Reaction.] Japanese Patent 212, Jan. 21, 1953; Chem. Abs., vol. 48, 1954, p. 308c.

A mixture of MeOH 50 and NiI₂ 5 parts is heated in an autoclave at 270° C. and 300 atm. pressure with CO for synthesis of AcOH and AcOMe. The product is distilled. The residue, containing the waste catalyst in an autoclave, is treated with MeOH and Cu powder (25 parts) and heated 20 minutes at 150° C. and 70 atm. with CO to give Ni(CO)₄ and CuI₂. The Ni(CO)₄ is recovered by distillation and the residue filtered to give CuI₂ to make 90-percent recovery of Ni and I.

SCRAP METALS, ALLOYS, AND COATINGS

1497. BURDICK, E. F. Removal of Nickel Coatings From a Metal Base. U. S. Patent 2,200,486, May 14, 1940; British Abs., 1946, p. B-1-40.

Ni is removed from an Fe-bearing base by dipping in concentrated HNO₃ containing a Cl compound (for example, NaCl or KCl) which is soluble in HNO₃. Preferred solutions comprise HNO₃, (d. 1.4-1.42) containing 0.056 gm. of NaCl per 100 ml. or 0.04-0.2 (0.08) part by volume of concentrated HCl, 1.18 sp. gr.

1498. DOWNIE, C. C. Reclamation of Small Amounts of Nickel and Cobalt. Min. Jour. (London), vol. 234, No. 5990, June 7, 1950, pp. 598-599; Eng. Index, 1950,

- p. 783; *Metals Rev.*, vol. 23, No. 8, August 1950, p. 21 (189-A).
- Various procedures are discussed, relating the nature of the initial treatments, roasting of speisses, and final concentration. A 20-percent Ni product is sold to wet-extraction works.
- 1499. FICAL, CELESTINO.** [Recovery of Nickel, Iron, Chromium, Cobalt, and Copper From Metallic Wastes.] Italian Patent 428,772, Jan. 3, 1948; *Chem. Abs.*, vol. 43, 1949, p. 8345a.
- Ni, Fe, Cr, Co, and Cu are recovered from wastes containing also alkali and alkaline earth oxides or metallic carbides by treatment with chlorine at 300°–600° C. Ferric chloride distills, and the other chlorides are extracted by leaching with water. The apparatus is described.
- 1500. FRANCIS-CARTER, C. F.** Commercial Methods of Stripping Chromium, Nickel, and Copper Deposits. *Jour. Electrodepositors' Tech. Soc.*, vol. 14, 1937–1938, pp. 17–24; *Chem. Abs.*, vol. 32, 1938, p. 7349^o.
- The following immersion or electrolytic methods of stripping electrodeposits are described (1) Cr from Ni plate by immersion in 10-percent HCl at 49°–79° C.; (2) Cr from steel anodically in NaOH, 7 oz. per gal.; or Na₂CO₃, 9 oz. per gal.; (3) Ni from Zn alloys, brass, bronze, steel, or Al anodically at 50–100 a. per ft.² in H₂SO₄, 67–78 percent by wt.; (4) Ni from brass anodically in 5 percent HCl; and (5) Cu from steel by immersion in a solution 64 oz. per gal. of CrO₃ and 7 oz. per gal. of H₂SO₄.
- 1501. HALL, E. C.** (assigned to Western Electric Co., Inc.). Removal of Metal Coatings From Brass. U. S. Patent 2,316,579, Apr. 13, 1943; *British Abs.*, 1945, p. B-I-238.
- Electrodeposited Ni and/or Cr is stripped from Fe alloys containing Ni to an extent of 45 percent by anodic treatment at 150–250 (preferably 200) a. per ft.² in a bath containing CrO₃, 16–64 (preferably 32) and H₂BO₃, 1–5 (preferably 3) oz. per U. S. gal. at 68°–85° C. (preferably 77° C.). A corrosion-resisting smut is also formed simultaneously.
- 1502. HALL, NATHANIEL.** Stripping Metal Deposits. *Metal Ind. (N. Y.)*, vol. 35, 1937, pp. 283–284; *Chem. Abs.*, vol. 32, 1938, p. 5757^o.
- Methods for removing Ni, Cr, Rh, Ag, Au, and Cu from different basis metals are described.
- 1503. HINE, FUMIO.** [Separation of Layers of Copper-Chromium and Copper-Nickel.] *Jour. Electrochem. Soc. (Japan)*, vol. 14, 1946, pp. 183–185; *Chem. Abs.*, vol. 44, 1950, p. 9832d.
- From the thin Cr-Cu or Ni-Cu layers deposited electrolytically on C electrodes, the Cu layers can be dissolved out alone electrolytically by 50-percent HNO₃. The Cr layer is most stable against solution in body-centered lattice and less stable in hexagonal close-packed. The Ni layer is most stable in a fibrous condition. The addition of sodium nitrate to the HNO₃ lessens solubility of Ni, but the presence of chloride ions in the HNO₃ increases solubility of Ni and Cr.
- 1504. ISHIDA, SHIRO** (assigned to Imperial Petroleum Oil Co.). [Recovery of Tungsten Carbide and Cobalt From Hard-Alloy Scrap.] Japanese Patent 5,158, Oct. 9, 1953; *Chem. Abs.*, vol. 48, 1954, p. 10,526a.
- Scrap WC-Co (200 gm.) containing 6 percent of Co is boiled for 16 hr. in 60 ml. of HCl (density, 1.15). The residue is washed with water to give 188 gm. of WC (93.8 percent W and 6.16 percent C) and the HCl solution cooled to give a 100-percent yield of CoCl₂.
- 1505. JONES, M. C. K.** (assigned to Standard Oil Development Co.). Recovery of Molybdenum, Vanadium, Nickel, and Zinc From Petroleum. U. S. Patent 2,383,972, Sept. 4, 1945; *Chem. Abs.*, vol. 40, 1946, p. 704^o.
- High-boiling fractions of Venezuela crude oils containing metals of the class consisting of Mo, V, Ni, and Zn are passed at 780°–900° F. and a space velocity of about 1.2 vol. per vol. per hr. over a solid reagent selected from the class of naturally occurring zeolites (hydrated alkali alumina silicates), which retains the metals.
- 1506. KAGAN, N. I.** [Extraction of Titanium and Cobalt From Wastes.] Russian Patent 69,629, Nov. 30, 1947; *Chem. Abs.*, vol. 44, 1950, p. 294a.
- Waste, such as is obtained in treating W-Ti-Co alloys, is fused with potassium-sodium carbonate and potassium nitrate. The W forms a soluble tungstate, the Ti forms potassium titanate, and the Co forms cobaltous cobaltic oxide. The tungstate is leached out, and the residue is treated with HCl. Co changes into its chloride, and the Ti precipitates as titanium basic hydroxide. The components are then separated in the usual manner.
- 1507. KROLL, W. J.** Scrap-Metal Recovery. U. S. Patent 2,396,793, Mar. 19, 1946; *Chem. Abs.*, vol. 40, 1946, p. 3093¹.
- Scrap or impure nickel is reduced to 60- to 100-mesh, suspended in a molten 40–60 mixture of sodium and potassium chlorides maintained at 500°–1,000° F. Chlorine is passed into the bath at a slow rate until a substantial amount of nickelous chloride is present; its passage is interrupted until the nickel chloride disappears (the metallic impurities replace the Ni), and this sequence is repeated until the bath is free of nickel chloride and contains suspended pure Ni.
- 1508. LAWARRÉE, H.** [Reclaiming Nonferrous Metals.] Belgian Patent 437,465, Dec. 23, 1939; *Chem. Abs.*, vol. 36, 1942, p. 2480^o.
- Nonferrous alloys are electrolyzed with the alloy serving as anode in a strongly acid bath capable of dissolving them. The potential is so adjusted that only Cu is deposited. Ni and Zn are then recovered from the spent electrolyte.
- 1509. ———.** [Reclaiming Copper, Nickel, and Other Nonferrous Metals.] Belgian Patent 438,814, Apr. 27, 1940; addition to Belgian Patent 437,465. *Chem. Abs.*, vol. 36, 1942, p. 2480^o; *Chem. Abs.*, vol. 36, 1942, p. 3108^o.
- The nonferrous alloy is used as a soluble anode. The voltage is such that only Cu separates. To the residue is added a predetermined amount of a carbonate not affecting the Ni; H₂S is passed through the solution to separate Zn and Ni; Zn is then claimed by electrolysis.
- 1510. LOEBERG, KARL** (assigned to Metallgesellschaft, A. G.). [Recovery of Metals and Alloys Used for Cladding Iron.] German Patent 809,106, July 23, 1951 (*Cl. 40a 15m*); *Chem. Abs.*, vol. 47, 1953, p. 5346d.
- A clad iron part is dipped into molten Mg; after a short time the cladding is completely dissolved, while Fe is not attacked. Iron parts clad with Cu, Ni, Zn, Cr, Cd, Sn, brass, bronze, or German silver are dipped into molten Mg at 700°–800° C. To avoid burning the Mg, protective covers of salts or inert gases are used. An iron part clad with an 84-percent-Cu, 16-percent-Ni alloy was dipped into molten Mg at 730° C. for about 10 min. The melt showed Mg 70.7, Cu 24.6, and Ni 4.6 percent; trace Fe. The melt was distilled in vacuo at 1,000° C. and 1 mm. Hg pressure, and the residue contained 2.8 percent Mg. Mg-Cu-Ni alloys may be used for prealloying Al alloys or as addition agents for cast steel to obtain a spheroidal structure.

1511. LUNDBYE, AXEL E. (assigned to Crowell-Collier Pub. Co.). Nickel Powder. U. S. Patent 2,463,190, Mar. 1, 1949; Chem. Abs., vol. 43, 1949, p. 3733d.

Ni powder is recovered electrolytically from the reclaim of scrapped printing presses, which contains Ni, Pb, Sn, Sb, and Cu. The metal is dissolved in 3 to 25 percent HCl, buffered at pH 4 with 2-5 oz. of boric acid per gal. The Cu, Pb, Sn, and Sb are precipitated with H_2S , and the Ni is obtained as a fine powder at the cathode. The current density is 3-5 a. per ft.², and the solution temperature is 68°-75° F.

1512. McCORMACK, RALPH, AND VILBRANDT, F. C. (Virginia Polytechnic Institute, Blacksburg, Va.). Distribution of Ferric Chloride Between Isopropyl Ether and Hydrochloric Acid in Stainless-Steel Salvaging Process. Virginia Polytech. Inst. Eng. Exp. Sta. Bull. Ser. 64, 1946, 10 pp. (see Miller and others, Chem. Abs., vol. 38, 1944, p. 1079⁶); Chem. Abs., vol. 41, 1947, p. 1971h.

In recovering Ni and Cr from stainless steel turnings, the rate of dissolution in HCl was increased by addition of ferric chloride. Data are given for extracting $FeCl_3$ from $FeCl_3$ -HCl- H_2O solutions with an equal volume of isopropyl ether. With 8 N HCl optimum distribution efficiency occurs in the range of 10.46-17.75 percent $FeCl_3$ (distribution efficiency of 158.0 and 170.0, resp.). The procedure is also recommended for recovering alumina from clay.

1513. METAL INDUSTRIES (LONDON). Stripping Defective Nickel Deposits. Vol. 66, 1945, p. 102; British Abs., 1947, p. B-I-315.

Ni is removed by making the article the anode in aqueous H_2SO_4 (density, 1.55), Pb cathodes and a 2-volt accumulator being used. When all Ni has been removed, no current flows, and the underlying Fe is unattacked.

1514. MEYER, W. R. (assigned to Enthone, Inc.). Removal of Metallic Coatings. U. S. Patent 2,561,065, July 17, 1951; Chem. Abs., vol. 45, 1951, p. 10,185h.

Metallic coatings are stripped from steel by solutions containing NaCN and $NaClO_2$. The concentration of NaCN may be 1 gm. per l. to saturation and $NaClO_2$ 5 gm. per l. to saturation and the temperature 130°-210° F. The composition is most suitable for removing Ni, but it also removes Cu, Zn, Ag, and Cd.

1515. MILLER, H. J. Scrap Metals. Supply and Industrial Applications. Metal Ind. (London), vol. 75, 1949, pp. 223-225, 251-253; Chem. Abs., vol. 44, 1950, p. 506h.

A review is given, listing sources and methods of utilizing Cu and Cu alloys, Al, Zn, Sn, and Ni scrap throughout the world.

1516. POLLACK, A., AND BRANDENBURGER, ROLF (assigned to Gerhard Collardin G. m. b. H.). [Removal of Plated Nickel.] German Patent 825,597, Dec. 20, 1951 (Cl. 40c 8); Chem. Abs., vol. 49, 1955, p. 3698c.

Ni-plated articles are treated as the anode in a H_2SO_4 bath containing organic or inorganic inhibitors, such as chromates, phosphates, silicates, hexamethylenetetramine, pyridine, quinoline, or thiourea derivatives to remove the Ni plate. By this means, an attack on the base metal is prevented, and a higher current density and voltage can be employed, for example, 10-15 a. per dm.² and 8-10 volts at 30°-40° C.

1517. SHERMAN, A. H., AND PESSES, M. Alnico Recovery Process Salvages Valuable Nickel, Cobalt. Iron Age, vol. 170, July 3, 1952, pp. 115-119; Metals Rev., vol. 25, No. 8, August 1952, p. 21 (249-A).

A practical method of recovering above waste metal grindings and skimmings in manufacture of permanent magnets is presented.

1518. THEWS, E. R. [Working Up Nickel Scrap and Droppings.] Giesserei, vol. 26, 1939, pp. 121-123; British Chem. Abs., 1939, p. B-617.

A discussion of pretreatment, melting, and purification of pure and alloy Ni scrap is given.

1519. TRAPP, G. J. Recovering Hard Metal Carbides From Sintered Masses. U. S. Patent 2,485,175, Oct. 18, 1949; Chem. Abs., vol. 44, 1950, p. 1882h.

Describes a process wherein sintered masses composed of a hard metal carbide, such as tungsten carbide, and a metallic bond (usually Co) are treated to recover the metal carbides and the metallic bond. The sintered masses are heated to a point above the melting point of the bond metal in a nonoxidizing, preferably reducing atmosphere. Thus the masses are made to swell, crack, and become porous throughout, and some of the bond metal may exude. In this way, after the masses are cooled, a very large area of bond metal is exposed to attack by acid. After removal of the bond metal, the sintered masses are readily subjected to mechanical reduction. The recovered carbide has a high combined C content and is of high purity. Experimental operation of the process showed that at least 95 percent of the original tungsten carbide and Co contents of the sintered masses can be recovered. When use is made of the recovered tungsten carbide to produce new sintered masses, the time of ball milling with Co can be reduced to one-third of the time required with new tungsten carbide. The method is applicable to sintered masses containing hard metal carbides and other bond metals in addition to Co.

1520. TZSCHASCHEL, HANZ. [Working Up German Silver Shot by Various Means.] Erzbergbau u. Metallhüttenw., vol. 2, 1949, pp. 161-168 and 212-214; Chem. Abs., vol. 43, 1949, p. 8327a.

Discusses recovery of Cu and Ni from German silver shot. The methods considered are the converter process, wet chemical methods, the carbonyl method, vaporizing, and distillation of melts.

1521. VELLER, R. L., AND MARTYNOV, P. G. [Extracting Rare Metals From Waste Iron Alloys.] Russian Patent 46,045, Feb. 29, 1936; Chem. Abs., vol. 32, 1938, p. 5767².

Fe-alloy wastes containing Co, W, etc., are heated, with stirring, in an oxidizing atmosphere and then subjected to the usual chemical treatment.

SPENT LIQUORS

1522. BANERJEE, N. G., AND BANERJEE, T. (National Metallurgical Laboratory, Jamshedpur, India). Recovery of Nickel and Zinc From Silver Refinery Waste Liquors. I. Recovery of Nickel by Electrodeposition. Jour. Sci. Ind. Res. (India), vol. 11B, 1952, pp. 76-78; Chem. Abs., vol. 47, 1953, p. 11,043g.

Zn was recovered as sulfide. Optimum conditions for Ni recovery were studied; at a pH of 11.6, 80-percent Ni recovery was accomplished in 3 hr. with a Ni cathode and stainless steel anode; at a pH of 6.2, 60 percent of the Ni was recovered. The metal was 99 percent pure.

1523. HIMEL, C. M. (assigned to Richfield Oil Corp.). Catalyst Recovery From Toluic Acid Mixtures. U. S. Patent 2,680,757, June 8, 1954; Chem. Abs., vol. 48, 1954, p. 10,958i.

The oxidation effluent from the liquid-phase oxidation of xylenes and xylene-containing aromatic fractions is held under pressure at 120°-200° C. for 1-15 minutes in the presence of water and inert gas. Soluble Co, Mn, or Ce catalyst is converted to a hydrated insoluble form and recovered by filtration for recycling to the oxidation zone. The filtrate contains less than 0.003 percent of Co. An example is given.

- 1524. JONES, F. D.** Pickle-Liquor Disposal, Ardmore, Pa. Iron Age, vol. 167, No. 10, 1951, pp. 88-91; Chem. Abs., vol. 45, 1951, p. 3314h.

Discusses manufacture and use of Ni and Cr salts, among other chemicals, recovered from the steel industry's annual 600 million gallons of spent pickle liquor.

- 1525. MOND NICKEL CO.** Recovery of Nickel From Solutions. British Patent 686,221, Jan. 21, 1953; Chem. Abs., vol. 47, 1953, p. 8331f.

An excess of an oxime, such as dimethylglyoxime, is added in a slurry or dilute solution at a pH of 3.15 to a dilute solution for Ni recovery. The precipitated Ni salt is centrifuged, then treated with 1-5 normal H_2SO_4 , which regenerates the oxime as a white solid and solubilizes the Ni. The oxime can be recycled. The acid treatment, to completely liberate Ni, must be done at less than pH 1.22. The oxime treatment can also be given to basic Ni solutions containing ammine complexes. The Ni oxime is separated, then treated with acid as above. This process is suitable for recovering small amounts of Ni.

- 1526. RIVIERE, A.** (assigned to Colin et Cie.). [Recovering Metals From Used Pickling Liquors.] French Patent 976,966, Mar. 27, 1951; Chem. Abs., vol. 47, 1953, p. 2119h.

Waste pickling liquors are treated with a base such as NH_4OH , and a stream of air to precipitate ferric hydroxide. Metals, including Ni and Co, are left in solution. Waste zinc oxide may be added to the liquor, preferably with a Mn salt present and also ammonium chloride, the ferric hydroxide precipitating.

- 1527. SIEGMANN, FRIEDRICH** (assigned to Deutsche Gold- und Silber-Scheideanstalt vormals Roessler). [Recovery of Metals From Plating Solutions.] German Patent 702,966, Jan. 30, 1941 (*Cl. 40a 11.01*); Chem. Abs., vol. 36, 1942, p. 736³.

Spent plating solutions containing Ni and Zn are precipitated with basic solutions. The nickel and zinc hydroxides are reduced with C—for example, charcoal, peat, or coke. The mixture is distilled in Fe retorts at 600°-1200° C.; this drives over the Zn, and the remaining metals are separated in the usual way.

- 1528. STANDARD OIL DEVELOPMENT CO.** Removal of Cobalt From Olefin, Carbon Monoxide, Hydrogen Reaction Mixtures. British Patent 682,177, Nov. 5, 1952 (*see U. S. Patent 2,596,920*, Chem. Abs., vol. 47, 1953, p. 1728f); Chem. Abs., vol. 47, 1953, p. 6434i.

- 1529. UNION CHIMIQUE BELGE, SOCIÉTÉ ANONYME.** [Working Up Waste Solutions.] German Patent 613,837, May 27, 1935 (*Cl. 40a 1301*); Chem. Abs., vol. 29, 1935, p. 7930¹.

Waste liquor containing Ni, Co, Cd, Zn, Cu, and Pb from the purification of Zn solutions is heated and oxidized at 300°-400° C., and the Ni, Co, and Cd present are leached out by the aid of zinc sulfate solution. The oxidized liquor is leached repeatedly, the Zn remaining.

- 1530. WISE, W. S.** (State Water Commission, Hartford, Conn.). The Industrial Waste Problem. IV. Brass and Copper, Electroplating, and Textile Wastes. Sewage Works Jour., vol. 20, 1948, pp. 96-102 (*see Chem. Abs.*, vol. 41, 1947, p. 3732d); Chem. Abs., vol. 42, 1948, p. 3882g.

Brass- and Cu-mill wastes consist of spent pickling wastes which contain H_2SO_4 , Cu, Zn, and Cr. These wastes have been treated by equalization, reduction of Cr^{6+} with SO_2 , neutralization with high-Mg lime, flocculation, sedimentation, and vacuum filtration of the sludge. Experiments are in progress that use ion-exchange beds to remove the Cu, Zn, and Cr and treatment of the regenerating solution to recover $NaCrO_4$.

by roasting and extracting the Cu and Zn electrolytically. Electroplating wastes contain Cu, Ni, Cr, Fe, and CN^- . These wastes have been treated with $FeSO_4$ and CaO, followed by sedimentation, lagooning, and chlorine to destroy CN^- . Textile wastes are treated chemically with alum, $FeSO_4$, $Fe_2(SO_4)_3$, CaO, and $CaCl_2$ to reduce the O consumed 60-80 percent and suspended solids 80-98 percent.

RECOVERY OF IRON FROM PLANT TAILINGS

- 1531. HIBBARD, H. D.** Steel From Mayari, Cuba, Ore. Manufacture and Uses of Alloy Steels. Bureau of Mines Bull. 100, 1916, p. 50.

A so-called natural Cr-Ni steel is now made from certain ores mined at Mayari, Cuba. The ores carry enough Ni to give 1.3-1.5 percent of Ni, and enough Cr to give 2½-3 percent of Cr in the crude Fe manufactured therefrom. When the Fe is converted into steel by the pneumatic or open-hearth processes, the Ni is practically all present in the steel, but the Cr is of necessity largely wasted by being oxidized.

Steel made in part from Mayari iron is giving good service in rails and particularly in track bolts.

- 1532. INCO.** Iron Ore to Be Recovered From Nickel Ores. Vol. 26, No. 3, 1954, pp. 7-8; Eng. Index, 1954, p. 757; Metals Rev., vol. 27, No. 4, April 1954, p. 34 (121-B).

Construction of plant in Copper Cliff area has been started for the production of byproduct iron ore from nickel ores in Sudbury district, Ontario. A new process developed by the International Nickel Co. will ultimately yield 1,000,000 tons of high-grade iron ore per year, in addition to Ni. A considerable portion of the ore's Fe content will be removed for treatment in the new plant before the ore goes to the smelter, thus releasing smelter capacity.

REFINING METAL; PYRO REFINING TO EXTREMELY PURE METAL

- 1533. CHALLANSONNET, JEAN** (Radiotechnique, Paris). [Nickel in the Manufacturing of Oxide Cathodes.] Congr. intern. cinquantenaire cathode oxydes, 1954: Le Vide 9, No. 51, 1954, pp. 22-27; Chem. Abs., vol. 49, 1955, p. 2274i.

Describes metallurgy of Ni; gives analyses of Mond, electrolytic, and Caledonian Ni; discusses properties due to additions of reducing elements. Phase diagrams are given for the systems Ni-Mg, Ni-Si, Ni-O, and Ni-S. Mg removes both O and S, whereas Si removes only O. Analyses are given of average American cathode Ni, of British nickel O (Wiggins), of German nickels K (Mg), L (Si), and N (Al), and of French nickels containing varying amounts of Mg and Si. Data are included on (1) the amounts of gas (O_2 , H_2 , CO , CO_2) extracted from Ni upon heating and (2) the sublimation deposits from cathodes at operating temperatures.

- 1534. DESCH, C. H.** [Preparation of Pure Metals.] Vorträge Hauptversamml. 1938 Deut. Gesell. Metallkunde, 1938, pp. 1-5; Met. Abstracts (in Metals and Alloys), vol. 10, No. 4, 1939, p. 204; Chem. Abs., vol. 33, 1939, p. 5785¹.

The difference between Al of extreme purity and slightly contaminated Al is remarkable. In the light of atomic distribution, the effect of impurities is difficult to explain. Because of surface tension, the dissolved element must be present in a different (mostly

higher) ratio at the grain boundaries than in the rest of the mass. The preparation of extremely pure Al, Zn, Fe, Cr, Mn, Mo, W, and Si is discussed. Pure Ni and Co are obtained by reduction of their oxides with C or H₂. An additional distillation of purified nickel carbonyl is also applied.

1535. GUILLET, LEON. [Some Problems of Modern Metallurgy.] *Génie civil*, vol. 109, 1936, pp. 1-7, 35-38, and 53-60; *Chem. Abs.*, vol. 30, 1936, p. 7075².

Discusses modern efforts to produce extrapure metals, to remove metallurgical defects, and of the progress in the mechanical, thermal, and chemical treatment with special reference to papers presented at the Paris conference last October. Gives detailed history of the difficulty of obtaining pure Zn, Al, and Ni, with tables and spectrograms. Describes some methods of the Cu and Fe industries, with photomicrographs. Includes a table showing the type of inclusions found in basic Martin steel and the treatment to remove them, also charts and photographs.

1536. KROLL, W. J. Vacuum Distillation of Metals. *Metal Ind.* (London), vol. 47, 1935, pp. 3-6, 29-31, 103-105, and 155-156; *Chem. Abs.*, vol. 30, 1936, p. 4131².

Nearly all elements can be sublimed at low pressures. As evaporation proceeds on the surface, the impurities collect on the surface and by diffusion the remaining portion homogenizes. Evaporation may be stopped by deposition of large amounts of impurities on the surface or by lack of diffusion power of the constituent to be volatilized. High-vacuum technique is discussed. In refining Be, the residue is enriched by Fe, C, Ni, Cr, and Ti, while Si, Cu, Al, and Mn go into the distillate, while in refining Fe, Ni is again found in the residue, and Co is not separated. In the refining of Ni, Cu is contained in the distillate, Co is not separated, and Cr is increased in the distillate and Fe in the residue.

1537. ZACKAY, V. F., AND KERSHAW, F. P. Melting and Refining of Relatively High-Purity Nickel. U. S. Atomic Energy Commission Rept. COO-6, 1950, 18 pp; *Nuclear Sci. Abs.*, vol. 4, 1950, pp. 418-419; *British Abs.*, 1952, p. B-I-1274.

Describes a laboratory vacuum induction furnace and a casting furnace, both of which can be evacuated or operated with any desired atmosphere and techniques developed for refining and casting ingots of relatively high purity (99.944 percent). The refining process removes or neutralizes the adverse effects of C, O₂, and S, by the use of carefully controlled atmospheres and additions of NiO. The S is dispersed as MgS. Careful control, maintenance of inert atmospheres in melting, and vacuum pouring give ingots of excellent quality.

REFINING TO SPECIFICATION METAL

1538. BELL TELEPHONE LABORATORIES, INC. Refining Nickel and Its Alloys. *British Patent* 304,371, Oct. 20, 1927; *Chem. Abs.*, vol. 23, 1929, p. 4665⁶.

Ni or alloys formed mainly of Ni are treated while molten with V, Ta, or Nb in small proportions, and V may be followed by a small quantity of Mg. Gives various details.

1539. BERNDORFER METALLWARENFABRIK ARTHUR KRUPP, A. G. Refining Nickel and Nickel Alloys. *British Patent* 340,632, Apr. 29, 1929 (see *German Patent* 526,369, Sept. 18, 1929; *Chem. Abs.*, vol. 25, 1931, p. 4214⁶); *Chem. Abs.*, vol. 25, 1931, p. 3954².

Deoxidation of Ni and Ni alloys is effected by adding Li (suitably in the form of an alloy containing Mg 85 and Li 15 percent) to the molten metal in small proportion (suitably 0.1 percent or less); this addition may be preceded by addition of Mn or Zn and may be followed by treatment with Mg.

1540. BOSCH, ROBERT, A. G. [Refining of Nickel and Cobalt.] *German Patent* 665,948, Oct. 6, 1938 (*Cl. 40a 43.70*) (see *British Patent* 499,677, Jan. 27, 1939, *Chem. Abs.*, vol. 33, 1939, p. 4950⁶); *Chem. Abs.*, vol. 33, 1939, p. 958⁴.

Commercial Ni and Co are decarbonized by heating to 1,000°-1,300° C., preferably in an oxidizing atmosphere.

1541. CLERC, H. J. M. E. Refining Molten Metals With Chlorine. *British Patent* 312,917, June 1, 1928 (see *French Patent* 669,109, June 1, 1928; *Chem. Abs.*, vol. 24, 1930, p. 1610⁶); *Chem. Abs.*, vol. 24, 1930, p. 815.

Cu, Ni, and Cu-Ni alloys, while molten, are treated with Cl₂. The metal may be covered with a layer of chloride, such as CaCl₂, or the stream of Cl₂ used may carry with it a volatile chloride; or the metal may be blown with O₂ in the presence of a chloride.

1542. CUSHING, DANIEL. Melting and Refining Bronze, Copper, Nickel, Tin, or Other Nonferrous Metals. U. S. Patent Reissue 17,347, July 2, 1929 (see original Patent 1,556,591, *Chem. Abs.*, vol. 20, 1926, p. 36); *Chem. Abs.*, vol. 23, 1929, p. 3895⁷.

1543. DISMANT, J. H., HAMILTON, H. J., FASELL, W. M., AND LEWIS, J. R. (University of Utah, Salt Lake City). Decarbonization of High-Carbon Cobalt Metal. *Jour. Metals*, vol. 4, 1952, *Trans.*, p. 884; *Chem. Abs.*, vol. 46, 1952, p. 8579h.

Co was decarbonized by (1) bubbling CO₂ up through the molten metal and (2) maintaining molten Co in a CO₂ atmosphere. In the first method, the gas was introduced below the surface of the molten metal by means of a quartz tube. A high-frequency induction furnace was used to keep the Co molten in both experiments. This kept the metal somewhat agitated and no doubt was an important factor in hastening decarbonization by the second method. Both methods decreased the C content to below 0.3 percent.

1544. FRUIHWIRTH, OTTO (assigned to Donau Chemie, A. G.). [Production of Metals From Their Halide Compounds.] *Austrian Patent* 169,067, Oct. 30, 1951; *Chem. Abs.*, vol. 46, 1952, p. 11,087d.

The metal chlorides (especially of Ni, Cr, B, Al, Si, Ti, V, Mn, and Be) are treated with NH₃ or organic bases. The additive compounds obtained are mixed with amalgams of reactive metals—for example, Na. The amalgam may be obtained in the reduction process itself, for example, by adding Hg during the electrolysis of a molten mixture of alkali halides and AlCl₃. The amalgam formed reacts with the residual AlCl₃ to give Al. The method is especially useful for obtaining metals (except noble metals) in pure form to be used as catalysts.

1545. HERMANN, HERBERT. [Refining Old Nickel.] *Chem. Ztg.*, vol. 58, 1934, pp. 481-482; *Chem. Abs.*, vol. 28, 1934, p. 5377⁶.

Theoretically the purification of secondary Ni is easy, but practical difficulties due to the high temperature and high affinity of Ni for S, O₂, and gases such as CO are met. Refining practice is outlined whereby As, C, Fe, Si, and Zn are removed by oxidation and the sulfides, oxides, and carbides by Mg. Pb can be removed by several oxidation treatments or by increase of the Zn content, followed by oxidation.

1546. INTERNATIONAL NICKEL CO., INC. Removal of Sulfur From Molten Nickel-Containing Masses. *British Patent* 585,587, Apr. 26, 1944; *British Abs.*, 1947, p. B-I-290.

Molten Ni or Ni alloy, preferably containing not more than 0.25 percent of Mn, is covered with a flux containing fluoride (CaF₂ 60-40 and CaO 40-60 percent), Mg, or Ca (or both) is introduced beneath the flux (5 parts of Ca or 1 part of Mg per 1 part of S), and the metal is kept molten for 5 min. to not more than 1 hr. Up

to 0.2 percent of S can be removed in 1 treatment. If more than one treatment is necessary, Mg is preferably used for the first and Ca for the last.

1547. INTERNATIONAL NICKEL CO., INC. [Removal of Sulfur From Nickel and Copper-Nickel]. German Patent 476,814, July 21, 1926; Chem. Abs., vol. 23, 1929, p. 3655⁵.

Si is removed from coarse Ni and Ni-Cu by a blast of gas which is weakly oxidizing, weakly reducing, or indifferent in action. The apparatus is described.

1548. LEPP, HENRY (two-thirds assigned to Compagnie générale d'électrometallurgie et des aciéries électriques d'Ugine). Purifying Fused Easily Reducible Metals Such as Copper and Nickel and Their Alloys. U. S. Patent 2,073,019, Mar. 9, 1937; Chem. Abs., vol. 31, 1937, p. 2990⁹.

Impurities of S and SO₂ are first removed in a furnace treatment with C and a slag to produce double barium-sodium carbonate, which is skimmed off; then H₂, CO, CO₂, N₂, and CN⁻ are oxidized by supplying an agent such as BaO₂.

1549. ———. [Contribution to the Problem of Melting and Refining of Metals.] Assoc. tech. fonderie (Paris) conf., Apr. 16, 1943; Chem. Abs., vol. 40, 1946, p. 4326⁵.

General, theoretical discussion of refining metals. S can be eliminated from liquid Cu only by saturating the metal with copper oxide, because SO₂ is soluble in liquid Cu, whereas in the case of Ni, S is eliminated and fixed as sulfite or sulfate in the basic slag. O and metal oxides are not considered so injurious to the quality of metals as the H₂ gas, especially when the gas comes from the humidity of the air.

1550. MANTELL, C. L. (assigned to Reduction & Refining Co.). Chemically Pure Cobalt. U. S. Patent 2,506,159, May 2, 1950; Chem. Abs., vol. 44, 1950, p. 6377f.

Raw Co₂O₃ is digested with 20° B. HCl, 420 lb. in a glass-lined, jacketed vessel, with stirring for 3 hr. at 100° C. The Cl₂ liberated is passed to a vessel containing CoCl₂ from a previous batch. The digested liquid is diluted to 144 gal. with cold H₂O. The Co concentration should be less than 7.5 percent. Dilute NH₄OH (1 part 26° B. NH₄OH + 4 parts H₂O by vol.) is added with stirring to a pH of 5.6 or 5.7; after 3 hr., the pH is brought to 5.8, and precipitated impurities are filtered off 1 hr. later. Ammonium chloride is added to make its concentration 5.5 percent, and 540 lb. of 26° B. NH₄OH is also added. Alternately, 675 lb. of NH₄OH may be used and no NH₄Cl. Chlorine from the first step is added, then 230 gal. of 20° B. HCl. Co content is 1.6–1.7 percent and should be kept below 2 percent. The precipitate [Co(NH₄)₂Cl₂] is filtered, washed with NH₄Cl (5–10 percent in H₂O), dried in air at 200°–220° F., and reduced to pure Co in Si boats by heating in H₂ and raising the temperature slowly to 1,000° F. HCl and NH₄Cl are recovered and recycled.

1551. MARCHANT, I. D., BANNING, L. H., AND HERGERT, W. F. Melting, Refining, and Granulation of Cobalt Powder. Bureau of Mines Rept. of Investigations 5133, 1955, 14 pp.

In refining Co metal to meet stockpile specifications it was necessary to lower the S and P content and also to alter the physical granule size. The usual practice for removing S is to flux with a high-lime slag under reducing conditions, and for removing P to maintain oxidizing conditions. In the first heats, two fluxes composed of lime, silica, and fluorspar were used; however, when analyses showed that the first flux removed both S and P, the use of the second was omitted. Immediately after the refining slag was skimmed off, a special flux of 4 lb. of silica with ½ lb. of fluorspar was spread over the molten bath to remove cobalt ox-

ide. Aluminum was the deoxidant. The melt, at 1,600° C., was poured into water for granulation. A large tonnage of powder was successfully treated to meet specifications with a very small percentage of Co lost to the slag.

1552. MERICA, P. D., AND KAYES, A. E. (assigned to International Nickel Co.). Nickel and Its Alloys, etc. British Patent 290,647, May 19, 1927; Chem. Abs., vol. 23, 1929, p. 813⁶.

To produce metal free from C and from gas, Ni-containing metal is melted; and, by the addition of nickel oxide or in other suitable manner, C present is completely oxidized, and the CO is boiled out of the metal. The nickel oxide is then reduced by a deoxidizer, such as Si, which does not form gaseous oxides, and Mn and Mg may be added before casting. Various details are given.

1553. MERLE, J. M. Refining Molten Metals Such as Pig Iron, Steel, Nickel, or Copper. U. S. Patent 2,355,885, Aug. 15, 1944; Chem. Abs., vol. 39, 1945, p. 55⁸.

A molten refining substance, such as special desulfurizing slag, a molten metal to be refined and another molten refining substance, such as a special dephosphorizing slag, are progressively deposited on a rapidly moving film-forming surface and drawn out into thin superposed films, and the products are collected. Various details of apparatus and modifications of operation and conjoint use of other refining agents are described.

1554. METALLGESELLSCHAFT, A. G. [Desulfurizing Nickel and Its Alloys.] German Patent 577,071, May 24, 1933; Chem. Abs., vol. 27, 1933, p. 3907.

The fused metal is treated with a small proportion of Li, which may be added as a Mg-Li alloy.

1555. MINING JOURNAL (LONDON). Cobalt Refining at Nkana, Northern Rhodesia. Vol. 239, Oct. 24, 1952, pp. 455–456; repr. from Rhokana Rev., vol. 1, Nos. 11 and 12; Metals Rev., vol. 25, No. 12, December 1952.

The various stages of Co purification at Nkana and processes used at the new company plant are discussed.

1556. NAUMANN, MAX, SCHLECHT, LEO, BUDDENBERG, OTTO, AND STAIGER, RUDOLPH (assigned to I. G. Farbenindustrie A. G. [Nickel.] German Patent 688,435, Feb. 1, 1940 (*Cl. 40a 43.01*) (see British Patent 509,076, Chem. Abs., vol. 34, 1940, p. 2777⁷); Chem. Abs., vol. 35, 1941, p. 3587⁷.

1557. OSBORG, HANS. Purifying Metals and Alloys. British Patent 387,685, Feb. 6, 1933; Chem. Abs., vol. 27, 1933, p. 4767.

Molten metals and alloys (for example, Fe, steel, Cu, Ni, and their alloys) are treated with up to about 2 percent of an alloy containing Li, Na, K, Ca, Sr, Ba, Ce, Th, and/or La. (See Chem. Abs., vol. 26, 1932, p. 3998.) In British Patent 387,724, Feb. 6, 1933, divided on Patent 387,685, the Li alloys are claimed. British Patent 387,725, Feb. 6, 1933, divided on 387,685. (See French Patent 722,554, Chem. Abs., vol. 26, 1932, p. 3998.) British Patent 387,726, Feb. 6, 1933, divided on 387,685. (See United States Patent 1,869,496, Chem. Abs., vol. 26, 1932, p. 5289.)

1558. ———. Metal Scavenging. Canadian Patent 331,597, Apr. 11, 1933; Chem. Abs., vol. 27, 1933, p. 3695.

Molten Cu, Fe, and Ni or their alloys are treated with a Li-Co alloy to scavenge and purify them. (See Chem. Abs., vol. 26, 1932, p. 3998.)

1559. ——— (assigned to Maywood Chemical Works). Purification of Metals and Alloys. Canadian Patent 340,603, Apr. 3, 1943 (see Chem. Abs., vol. 27, 1933, p. 4767); Chem. Abs., vol. 28, 1934, p. 4028⁸.

Metals including Cu, Fe, and Ni and their alloys, while in a molten state, are treated with 2 percent of a Li-Ca-Si composition. The metal is scavenged and purified, and the properties are improved.

1560. PECE, I. L., CHIERCHINI, ANSELMO, AND CERRATO, VITTORIO. [Purifying Melted Metals.]. Italian Patent 458,347, July 10, 1950; Chem. Abs., vol. 45, 1951, p. 9452f.

Ten different compounds are given for purifying Al and its alloys, melted Al and Al wastes, Cu and its alloys, Zn and its alloys, Ni and its alloys, and Sn and its alloys and for eliminating Mg from melted Al, Mn from Cu alloys, and S from cast iron and steel.

1561. PERRIN, R. M. V. (assigned to Société d'électrochimie, d'électrometallurgie et des aciéries électriques d'Ugine). Purifying Crude Nickel. U. S. Patent 2,049,721, Aug. 4, 1936; Chem. Abs., vol. 30, 1936, p. 6316⁴.

The molten metal to be purified is violently intermixed with a molten and very fluid slag capable of extracting the impurities to be eliminated from the Ni, so that the slag is finely dispersed in the molten metal and produces an almost instantaneous elimination of the impurities.

1562. RICHARDS, E. T. [Refining Nickel.] Metallbörse, vol. 22, 1932, pp. 673-674; Chem. Abs., vol. 26, 1932, p. 4017.

The effects of S, C, Si, H, O, etc., upon the properties of Ni, and methods for refining the metal by use of measured quantities of Mg, C, Mn, etc., as well as by heat treatments in oxidizing or reducing atmospheres are given.

1563. SCHMAL, LEO. [Remelting of Nickel for the Production of Compact Pure Nickel Plates for Anodes.] Metall., 1931, pp. 61-64; Chem. Zentralbl., vol. II, 1931, p. 304; Chem. Abs., vol. 26, 1932, p. 4280.

Crude Ni in cubes, bars, or granular form is furnished by the smelter 98-99 percent pure, the particularly injurious impurities being Fe, As, S, and C. Because of its high melting point, Ni readily forms the oxide, which dissolves in the metal with the inclusion of gases. Mg (0.05 percent), Mg-Al alloy, or Mg-Ni alloy is used for deoxidation. A Mg-Mn-P alloy in the proportion 5 : 3 : 2 is very good. P alone in slight excess makes the Ni brittle. During remelting the bath surface must be protected from oxidation and gas absorption by a glass cover. Ni readily absorbs C from the melting pots with the formation of fine pores which render the metal useless. Therefore, the melting pots or crucibles must have linings rich in clay. Casting molds are best made of hematite pig iron covered inside with graphite and linseed oil. Fine-pored crucibles lined with chamotte are placed in the founding molds. Shaft crucible furnaces are used; oil furnaces are not suitable, and electric ones are too expensive to operate.

1564. SMITH, W. S., GARNETT, H. J., AND RANDALL, W. F. Refining Magnetic Metals and Their Alloys. British Patent 368,780, Dec. 6, 1930; Chem. Abs., vol. 27, 1933, p. 2125.

Magnetic metals or alloys, particularly Fe, Ni, and their alloys, are refined by subjecting the molten metal in a closed container to the action of a predetermined amount of O₂ or O₂-containing substance in conjunction with a blast of inert gas, the gaseous products of the oxidation being withdrawn under reduced pressure.

1565. SOCIÉTÉ D'ÉLECTROCHIMIE, D'ÉLECTROMÉTALLURGIE ET DES ACIÉRIES ÉLECTRIQUES D'UGINE. [Nickel]. French Patent 765,165, June 4, 1934; Chem. Abs., vol. 28, 1934, p. 6693⁷.

Crude and waste Ni are purified by a violent and intense beating of the fused Ni with previously fused

and very fluid slag. To remove S, a slag containing alkali or alkaline earth metal oxides and a small amount of SiO₂ or TiO₂ (to increase fluidity) is used. C may also be present. A number of slags, varying in composition according to the impurity to be eliminated, may be used in succession.

1566. ———. [Refining Nickel.] German Patent 594,651, Mar. 20, 1934 (*Cl. 40a 43.70*); Chem. Abs., vol. 28, 1934, p. 4365⁴.

Crude or waste Ni is refined by mixing it in the fused state with a watery slag. A slag containing SiO₂, TiO₂, and oxidic compounds of alkali or alkaline earth metals is suitable.

1567. STERN, MAX. Low-Carbon Nickel-Iron Alloys and Nickel Steels. British Patent 571,593, Aug. 31, 1945; Chem. Abs., vol. 41, 1947, p. 2687e.

Impurities and undesirable components are removed from Fe-Ni alloys and Ni steels by adding nickelous oxide or nickelous oxide-containing materials to a molten bath of Fe-containing material in such proportions that C, Si, Mn, P, S, and Cr, if present, are mainly eliminated and the Ni is incorporated in the purified molten bath.

1568. THEWS, E. R. Remelting and Refining of Scrap Nickel. Metal Ind. (London), vol. 46, 1935, pp. 265-268; Chem. Abs., vol. 29, 1935, p. 3270⁷.

Impurities in Ni impair its mechanical properties, causing embrittlement and other difficulties much greater than the proportionate impurity content. The chief impurities to cause concern are S, C, SiO₂, and O and other absorbed gases. Among furnaces to be used in the purification process, the reverberatory and the electric furnace are preferred because of greater temperature control and fewer gas problems. Mg is to be preferred over Mn in removing S embrittlement, as the magnesium sulfide spheres distribute themselves throughout the Ni grains, while manganese sulfides segregate at grain boundaries. The use of cover layers, gas-absorption prevention, and purifying procedures in general are discussed.

1569. ———. [The Use of Alkaline Salt Mixtures, Chlorine Gas, Chlorides, etc., in the Refining of White Metals and Alloys.] Metallurgie u. Gless. Tech., vol. 2, 1952, pp. 298-304; Chem. Abs., vol. 47, 1953, p. 6837i.

Review with bibliography.

1570. TULLIS, D. R., AND OAKLEY, P. Refining Non-ferrous Metals and Alloys. British Patent 351,177, Mar. 8, 1930; Chem. Abs., vol. 26, 1932, p. 2690.

In refining metals, such as Al and its alloys, Cu, Ni, Pb, and alloys of these metals, a volatile oxychloride such as vanadium oxychloride, derived from a grain-refining metal, is introduced into the molten metal or alloy, together with Cl₂ or a chlorine-evolving substance or other reagent capable of removing from the metal the O given off by the oxychloride.

1571. VAN ARKEL, A. E. [Production of High-Melting Metals by Thermal Dissociation of Their Compounds.] Metallwirtschaft, vol. 13, 1934, pp. 405-408; Chem. Abs., vol. 28, 1934, p. 5011⁴.

Metals can be produced in very pure form by heating one of their compounds in an evacuated vessel, provided the compound will dissociate into the metal and gas at a temperature below the melting point of the metal. In this method the metal is not melted and does not come in contact with impurities. Tungsten can be prepared by heating WCl₆ in an evacuated pyrex tube to about 300° C., which causes it to volatilize. In the upper part of the tube, a W wire is heated electrically to 1,400° C. This temperature causes the WCl₆ to dissociate, pure W is deposited on the wire, which grows uniformly, and Cl₂ gas is liberated. The Cl₂ combines with the W powder that has been placed in

the tube, and the process continues until the W powder is used up. By similar processes, Ni can be produced from Ni carbonyl. The temperatures to which the compounds and the metallic wires should be heated and the means for removing the gas formed are given. It is also possible to produce some alloys and compounds by this method.

1572. WERNER, O. (Materialprüfungsamt, Berlin-Dahlem, Germany). [Desulfurizing Nickel.] *Metall.*, vol. 5, 1951, pp. 323-328 and 381-384; *Chem. Abs.*, vol. 45, 1951, p. 10,160h.

Hot working of cast Ni is only possible when the melts are treated to remove S. The mechanism by which the presence of S interferes is discussed. Over 0.005 percent of S is harmful. Desulfurizing can be accomplished by the adding of small quantities of Mg, which form MgS. This is light and partly floats on the surface, but the larger part remains in the bath; however, it does not separate along the grain boundaries and does not interfere with hot forming. The desulfurizing process, therefore, consists more of converting S into a harmless form than actually removing it. Photomicrographs are shown.

1573. WEVER, FRANZ (assigned to Kaiser-Wilhelm Institut für Eisenforschung). Refining Metals and Alloys. U. S. Patent 1,745,464, Feb. 4, 1930; *Chem. Abs.*, vol. 24, 1930, p. 1611¹.

Refining of Ni or Co or other metals or alloys is carried out in a high-frequency induction furnace by smelting the metal with slags which under the conditions of temperature and turbulence of the operation have a greater affinity for an impurity than for the fundamental metal (high turbulence being imparted to the materials in the furnace).

REFINING WASTE AND SCRAP MATERIALS

1574. DANILOV, A. [The Remelting of Chromium-Containing Wastes in Electric Furnaces.] *Novosti Tekhniki* (U. S. S. R.), vol. 9, 1940, No. 7-8, pp. 23-24; *Chem. Zentralbl.*, vol. I, 1941, p. 817; *Chem. Abs.*, vol. 37, 1943, p. 37⁶.

To recover the valuable alloying constituents, such as Cr, Mo, Ni, W, and V, from the wastes of casting, rolling, and machining high-alloyed tool steels, these wastes were remelted in an induction furnace with an acid lining. The charge consisted of 60-70 percent waste and 30-40 percent soft Fe. The C content of the charge was about 0.5 percent. The composition of the slag used was: CaO 20, MgO 16, Al₂O₃ 30, SiO₂ 20, Cr₂O₃ 3, MnO 5, and FeO 6 percent. The advantage of the use of an induction furnace over other furnaces is that in it the loss of valuable alloying elements such as W and V, is slight.

1575. KROLL, W. J. Refining Nickel. U. S. Patent 2,396,792, Mar. 19, 1946; *Chem. Abs.*, vol. 40, 1946, p. 3093⁶.

Finely divided Ni, containing impurities such as Cu, Fe, Co, Cr, Zn, and/or Mn, is added to a fusion mixture containing 60 percent of KCl and 40 percent of NaCl with NiCl₂ in excess (25-50 percent) and maintained at 650°-750° F. The impurities displace Ni in NiCl₂, and pure Ni results. The process is useful for treating Ni scrap, selective removal or several treatments being employed. In United States Patent 2,396,794, Ni containing up to 2 percent of Cu, Co, Fe, Cr, Zn, and/or Mn is reduced to 100-mesh, briquetted with 100-mesh anhydrous NiCl₂, and heated to 500°-1,000° F. The product, after being washed with water to remove the remainder of the metal chlorides, is pure Ni, the impurities having replaced the Ni in the NiCl₂.

1576. POLAND, FRANK F. High-Temperature Furnace in Distilling and Refining Metals. *Materials and Methods*, vol. 23, 1946, pp. 710-712; *Chem. Abs.*, vol. 40, 1946, p. 3082⁷.

Gives descriptions and illustrations of a graphite-resistor furnace to recover Cu-Ni from Ni-Ag by smelting and condensing Zn.

1577. SHERMAN, A. H., AND PESSES, MARVIN (Alter Co., Davenport, Iowa). Nickel, Cobalt From Alnico Scrap. Alnico Recovery Process. *Iron Age*, vol. 170, 1952, No. 1, pp. 115-119; *Chem. Abs.*, vol. 46, 1952, p. 7484i.

Ni, Co, and Cu are recovered from the waste dumps of Alnico-magnet manufacture as follows: Cleaned and dried crushings and grindings are magnetically sorted, and then rebled to correct proportions. Al is added as a deoxidizer. Quartz and Na₂SiO₃ are added to produce a marketable slag, and the mix is melted. Just before pouring, iron oxide is added to remove excess C and Si. Heats of 3,000 to 4,000 lb. are poured as shot or ingot and shipped to magnet makers.

1578. SOCIÉTÉ D'ÉLECTROCHIMIE D'ÉLECTROMÉTALLURGIE ET DES ACIÉRIES D'UGINE. Refining Nickel. British Patent 432,439, July 26, 1935 (*see* French Patent 765-165, *Chem. Abs.*, vol. 28, 1934, p. 6693⁷, and German Patent 594,651, *Chem. Abs.*, vol. 28, 1934, p. 4365³); *Chem. Abs.*, vol. 30, 1936, p. 420⁸.

Crude or waste Ni is refined by mixing it in the fused state with a fluid slag. A slag containing SiO₂, TiO₂, and oxidic compounds of alkali or alkaline earths is suitable. Crude and waste Ni are purified by a violent and intense beating of the fused Ni with a previously fused and very fluid slag. A number of slags in succession may be used, varying them to remove impurities.

1579. THEWS, E. R. [Working Up Nickel Scrap and Waste in the Foundry.] *Glessner*, vol. 28, 1939, pp. 121-123; *Chem. Abs.*, vol. 33, 1939, p. 6763¹.

In melting scrap to purify it, the electric arc furnace is not suitable because of carburization, but the low-frequency furnace is satisfactory. The crucible should be of refractory clay or lined with it and able to stand 1,550° C. The Ni-containing charge is melted down, the crucible covered, and the slag (calcined sodium and potassium carbonates) removed; and 0.15 percent Mn, and, after 2 minutes, 0.05-0.1 percent Mg are added. If the Ni is free from S, Mn can be used alone and keeps the oxidation from going too far. The greater heat produced by Mg thins the melt and lets the MnS formed rise. If a 1:1 Mg-Al alloy is used, 0.125 percent is enough to completely deoxidize and desulfurize. The old slag must be removed, and a new calcium silicate slag put on before deoxidation. Ni scrap containing Cu and Zn can be used for alloying.

REFINING METAL; ELECTRO REFINING TO EXTREMELY PURE METAL

1580. HÄNSEL, GÜNTHER [Electrolytic Methods for Obtaining the Purest Metals From Ores and Raw Metals.] *Electrotech. Ztschr.*, vol. 64, 1943, pp. 579-584; *Chem. Zentralbl.*, vol. I, 1944, j. 795; *Chem. Abs.*, vol. 39, 1945, p. 3208⁷.

The effects of impurities on the properties of metals and their analytical determination are surveyed. The theoretical fundamentals of electrorefining of metals which represent the best method now available for obtaining the purest metals are discussed. The electrorefining of Cu, the electrowinning of Zn from aqueous solutions, and the molten-bath electrolysis for Al, as

well as the subsequent refining methods, are treated in detail. Brief reference is also made to valuable byproduct metals (Ag, Au, Pt, Pd, Bi, and Cd). Ni and Co may be refined to 99.9-percent purity, with a consumption of 2,800 kw.-hr. of electricity per ton of metal.

1581. KERSHNER, K. K., HOERTEL, F. W., AND STAHL, J. C. (Bureau of Mines, Rolla, Mo.). Experimental Production of High-Purity Cobalt. Bureau of Mines Rept. of Investigations 5175, 1956, 12 pp.

Co with a purity of 99.99 percent with reference to metallic impurities has been produced. An electrolyte was purified by precipitation of contained impurities, using Na_2CO_3 and also 1, 2-cyclohexanedione oxime, followed by a preliminary purification electrolysis. Co was then precipitated and dissolved for the final electrolysis, which deposited metal of extremely high purity. Finally, ingots were poured from a melt in a vacuum induction furnace (27 refs.).

1582. MONSELISE, G. G. [Electrolytic Production of Very Pure Metal From Its Alloys.] *Helv. chim. acta*, vol. 22, 1939, pp. 935-937; *Chem. Abs.*, vol. 33, 1939, p. 7668⁵.

A two-stage electrolysis operation is described. In the first, conditions are specified for dissolving the Ni-containing anode and for loosely depositing Cu, allowing noble-metal slimes to settle; the last traces of Cu are removed by Ni cementation, and Fe is oxidized and precipitated. In the second electrolysis, conditions are detailed for obtaining a good deposit of Ni metal, using a graphite anode and Ni cathode.

1583. OLDACH, C. S., AND LANDAU, RALPH. Cobalt Electrolytically Refined. *Metals and Alloys*, vol. 17, 1943, pp. 967-968; *Chem. Abs.*, vol. 37, 1943, p. 4632⁶.

The commercial metal (98.4-98.7 percent Co) can be improved by electrolytic refining to 99.76 percent Co. The metal is supplied as rondelles (cylinders $\frac{1}{2}$ by $\frac{1}{2}$ in.). The commercial Co was made the anode by placing in contact with Pt sheet on the bottom of a beaker and connecting the lead to the Pt. A stainless-steel cathode was rotated 60-100 r. p. m. at a current density of 4.5 a. per dm.² The bath contains H_2BO_3 , CoSO_4 , and NaCl. The pH is kept at 4.5-5.0 and the temperature at 55° C. The current efficiency at both electrodes is about 95 percent.

REFINING TO SPECIFICATION METAL

1584. BOGITCH, B. [An Electrolytic Refining Process for Nickel.] *Compt. rend.*, vol. 188, 1929, pp. 328-329; *Chem. Abs.*, vol. 23, 1929, p. 2106⁷.

Anodes containing about 10 percent of Cu, Fe, C, S, As, and O yields cathodes containing 99.9 percent of Ni plus Co. A two-compartment cell is used. The electrolyte, a solution of NiCl_2 of specific gravity 1.2, flows from the cathode chamber to the anode chamber and thence to a purification tank, where $\text{Ni}(\text{OH})_2$ is added to precipitate Fe, As, Co, etc. The temperature is kept at 65° C. Some of the Cu remains with the anode mud, but the bulk must be removed by a special (not described) electrolytic process. The deposit peels from plane starting sheets, but satisfactory results are obtained by plating on pure Ni wire 0.5 mm. in diameter. The Ni salt held by the filter cake is used to prepare the nickelic hydroxide. The method of preparation is not given, nor are the current density, energy consumption, materials of construction, treatment of anode mud, etc.

1585. BRYK, P. B., AND AABNISALO, S. A. (assigned to Outokumpu Oy.). [Electrolytic Purification of Nickel From Nickel Matte.] *Swedish Patent* 124,

283, Mar. 15, 1949; *Chem. Abs.*, vol. 43, 1949, p. 8919h.

Pure Ni is obtained by electrolysis in two stages, in the first of which the Ni matte is used as the anode in a cell containing neutral or weakly acid Ni solution and provided with a porous diaphragm between anode and cathode. The electrolyte is made to flow continuously from the cathode compartment to the anode compartment through the diaphragm. The Cu-containing electrolyte thereby obtained is then passed to a second stage, where it is electrolyzed with a Ni matte anode but no porous diaphragm, so that the Cu is deposited on the cathode with the Ni. The electrolyte, which is then free from Cu, is returned to the cathode compartment of the first cell in which pure Ni is deposited on the cathode. In the preferred form, several cells are used in the second stage, and the electrolyte is then passed through them in series, the anode of the first cell or cells being of Ni matte and the last cell Cu-free Ni.

1586. BUCK, M. P. (assigned to International Nickel Co. of Canada, Ltd.). Carbon-Containing Nickel. *Canadian Patent* 454,186, Jan. 18, 1949; *Chem. Abs.*, vol. 43, 1949, p. 7358e.

Ni is electrodeposited at a cathode from a Ni electrolyte containing acetylene, and the product is heated in a protective atmosphere to temperatures at which diffusion of the elemental C occurs.

1587. — (assigned to International Nickel Co. of Canada, Ltd.). Modified Electrolytic Nickel. *Canadian Patent* 454,187, Jan. 18, 1949; *Chem. Abs.*, vol. 43, 1949, p. 7358d.

A mixture of powdered Ni with one or more of Li, Be, Na, Mg, and Al is molded to form an integral starting sheet, the sheet is immersed as cathode in a Ni electrolyte, a layer of Ni is electrodeposited on the sheet, and the sheet is removed and heated to between 400° F. and the temperature of incipient fusion of Ni to cause the modifying agent to diffuse from the sheet into the electrodeposited Ni.

1588. COOK, W. J. BARKER, W. V., AND TUCK, J. H. (assigned to International Nickel Co., Inc.). Electrorefining of Nickel. *U. S. Patent* 2,686,757, Aug. 17, 1954; *Chem. Abs.*, vol. 49, 1955, p. 2224b.

Commercially acceptable cathode Ni, substantially free of honeycombing, is produced by electrolysis of aqueous sulfate-chloride electrolytes, to which have been added 0.0003-.001 gm. per l. of at least 1 terminally substituted polyethylene oxide condensate. These are selected from a group consisting of: (1) A polyethylene oxide condensate of 3-methyl-4-octylphenol containing 8-11 moles of ethylene oxide per mole and (2) a polyethylene oxide condensate of dodecyl alcohol containing 4-6 moles of ethylene oxide per mole. Electrolysis is carried on at a pH of 3.0-5.0, at a bath temperature of 100°-160° F. and at a current density of 5-25 a. per ft.² The electrolyte contains Ni 40-70, Na 12-30, chloride ion 18-55, sulfate ion 65-115, and H_2BO_3 15-25 gm. per l.

1589. FALCONBRIDGE NIKKELVERK AKTIESELSKAP. [Refining Nickel by Electrolysis.] *Norwegian Patent* 57,531, Jan. 25, 1937; *Chem. Abs.*, vol. 31, 1937, p. 4909⁸.

Ni is deposited electrolytically (for example, onto a plate of Al), is stripped off, and is then treated for several hours in an acid bath consisting, for example, of 1 percent H_2SO_4 at 50° C. This Ni plate is then introduced, wet with acid, into the electrolytic refining bath for the deposition of the refined Ni.

1590. FEDOT'EV, N. P. [Electrolytic Refining of Nickel.] *Jour. Appl. Chem. (U. S. S. R.)*, vol. 15, 1942, pp. 5-24; *Chem. Abs.*, vol. 37, 1943, p. 1934⁹.

A review of the literature and experience in plant operation indicate that increase in current efficiency is favored by increase in NiSO_4 concentration, decrease in H_2SO_4 concentration, increase in cathode-current density, and increase in bath temperature. Since the upper limit of pH is 6.5, at which hydrolysis of NiSO_4 begins, in practice a pH of 5.5 is used at 50°–60° C. and at a fairly wide range of current density. Impurities, such as Cu and Fe, which may enter the solution from the anode, may deteriorate the Ni deposit. Fe raises the hardness of the deposit and increases strains in it, while Fe concentration of 3 to 4 gm. per l. causes the Ni deposit to crack and peel; Cu less than 0.5 percent in the Ni deposit does not affect the appearance, but at higher concentrations the deposit shows dark spots and spongy growths. This may occur as a result of faulty diaphragm operation, which permits access of Cu from the anolyte. Zinc at over 0.01 gm. per l. causes dark spots. The electrolyte solution must contain a high enough concentration of Ni ions, it must be free of impurities, it must contain chlorides to avoid passive conditions of the anodes, and proper pH must be maintained by buffers, such as H_3BO_3 . Sodium salts give better Ni deposits than do ammonium salts. Conductivities of the standard Ni solutions were measured.

1591. GRONNINGSÆTER, A. M. (assigned to Falconbridge Nickel Mines, Ltd.). Electrolytic Refining of Nickel. U. S. Patent 2,001,385, May 14, 1935; Chem. Abs., vol. 29, 1935, p. 4272².

In depositing Ni on the Ni-starting sheets, the starting sheets, before being introduced into the electro-deposition cell, are subjected to the action of dilute acid, such as 1-percent H_2SO_4 , solution of sufficient strength to effect dissolution of basic Ni compounds on the surface of the sheets but so dilute as not to attack, to any appreciable extent, the metallic Ni, even when left in contact with it for several hours.

1592. — (assigned to Falconbridge Nickel Mines, Ltd.). Production of Malleable and Annealable Nickel Directly by Electrolysis. U. S. Patent 2,115,019, Apr. 26, 1938; Chem. Abs., vol. 32, 1938, p. 4446⁵.

In the electrolysis, a highly purified Ni electrolyte is used, at a temperature of 25°–45° C. and a current density not greater than 1 a. per dm.², maintaining the pH as high as possible without occurrence of precipitation.

1593. — (assigned to Falconbridge Nickel Mines, Ltd.). Malleable and Annealable Nickel. U. S. Patent 2,478,189, Aug. 9, 1949; Chem. Abs., vol. 43, 1949, p. 8289h.

Describes improvements in the electrolytic refining of Ni to produce smooth, malleable, and annealable cathodes substantially free from berries and pits. The cathode is surrounded by a porous bag and suspended in a purified and circulating aqueous NiSO_4 electrolyte free from Pb, As, and organic matter and containing Ni 25, Na_2SO_4 20–25, and H_3BO_3 25 gm. per l. at a pH of 1.5–4 and 40°–80° C.; current is 0.5 to 5 a. per dm.² Air bubbles are introduced in the bottom of the bag to stir the electrolyte next to the cathode vigorously; this removes the berry- and pit-forming H_2 bubbles and berry-forming solid impurities and prevents the electrolyte adjacent to the cathode from becoming basic enough to form objectionable berry impurities on the cathode.

1594. HAIDEGGER, ERNO. [Electrolytic Production of Nickel.] *Banyasz Kohász Lapok*, vol. 83, 1950, pp. 571–578; Chem. Abs., vol. 45, 1951, p. 6089h.

Crude granulated Ni containing Ni–96, Cu–2, and Fe–1 percent and some Si, C, and S, and Mn was heated in graphite crucibles, rolled into sheets, and refined by electrolysis with various electrolytes. The

current efficiency and quality of the deposited Ni were poor when a cool liquid was electrolyzed at 125 v. and 70 amp. This is explained by the strong chemical polarization of Ni at room temperature, which leads to reactions of higher potentials such as development of H_2 and O_2 . Best results were obtained at 60° C. The material transport in all electrolytes examined was effected by NiSO_4 . The addition of H_3BO_3 was advantageous, since it stabilized the pH. The optimum pH should be established empirically. When a catholyte is processed at a pH that is too low, the Ni deposit contained NiO in the form of black dots, and the cathode had bubbles on the surface. The structure of the deposited Ni layer was finer than with a chloride electrolyte, using a sulfate. When cast anodes were used in place of rolled anodes, solution took place more readily. Metallic contaminations of the anode, except Co, did not deposit on the cathode if certain precautions were observed. The presence of NiCl_2 or KCl prevented the passivity of the anode. After processing, the spent electrolyte in the anodic area was recovered in two phases. The liquid was aerated or treated with $\text{Ni}(\text{OH})_2$ to remove Fe as hydroxide. Co was then precipitated by addition of $\text{Ni}(\text{OH})_2$, and NaClO , and the $\text{Co}(\text{OH})_2$ precipitate was removed by filtration. Further processing was required to separate precious metals, chiefly Pt.

1595. LEVIN, A. I. Electrorefining of Nickel Containing Copper. *Jour. Appl. Chem. (U. S. S. R.)*, vol. 25, 1952, pp. 697–703 (English trans.) (see Chem. Abs., vol. 47, 1953, p. 7917g); Chem. Abs., vol. 48, 1954, p. 5002i.

1596. — (S. M. Kirov, Ural Polytechnic Institute). [Electrorefining of Nickel Containing Copper.] *Zhur., Prikladn. Khim.*, vol. 25, 1952, pp. 616–625; Chem. Abs., vol. 47, 1953, p. 7917g.

Cu anodes contained a considerable content of Ni from 0.1–3 percent as (1) a solid solution, (2) as $6\text{Cu} \cdot 0.8\text{NiO} \cdot 2\text{Sb}_2\text{O}_3$, or (3) as NiO. Owing to intercrystalline corrosion, more Ni dissolved than corresponded to the electrochemical equivalent, decreasing the conductivity of solution. The anode was passivated, as seen from measurements of anode potential and anode polarization. The circulation of liquid was impaired. Increase of circulation speed to 12–18 l. per min. and periodic or continuous filtering of the electrolyte improved the solution of the anode and lessened growths on the cathode.

1597. MOND NICKEL CO., LTD. Electrolytic Purification of Nickel. British Patent 569,444, May 24, 1945; Chem. Abs., vol. 41, 1947, p. 5036e.

Impure Ni containing Fe and Cu is anodically dissolved in an electrolyte consisting principally of sulfate ions but also containing chloride ions. The electrolyte is then treated first for the oxidation and precipitation of Fe and then for the precipitation of Cu. The purified electrolyte is used in the cathodic deposition of Ni.

1598. MORISHITA, ICHIN. [Electrolytic Refining of Nickel.] Japanese Patent 2258, June 18, 1952; Chem. Abs., vol. 47, 1953, p. 6283c.

The electrolysis of NiSO_4 is carried out with an insoluble anode and a diaphragm in an alkali solution as the anolyte.

1599. PEEK, R. L., AND KNITTEL, C. A. (assigned to International Nickel Co., Inc.). Refining Nickel. British Patent 379,322, Aug. 15, 1930 (see Canadian Patent 323,286, Chem. Abs. vol. 26, 1932, p. 3368); Chem. Abs., vol. 27, 1933, p. 3185.

1600. RENZONI, L. S. (assigned to International Nickel Co.). Electrorefining of Nickel. U. S. Patent 2,394,874, Feb. 12, 1946; Chem. Abs., vol. 40, 1946, p. 3062².

Impure Ni is anodically corroded in a solution containing Ni 40-60, Na 20-30, Cl 27-30, and SO_4 ion 71-120 gm. per l. and which is maintained at a pH of 4-5. The anode and cathode compartments are separated by a pervious diaphragm. The impure anolyte is continuously removed. It contains Fe, Cu, Co, As, and Pb, in the reduced state, the amount of Cu being 3-4.5 times that of Fe. Air is passed through it, oxidizing the Cu and Fe. The latter is separated as $\text{Fe}(\text{OH})_3$, without substantial change of pH. The anolyte is then treated with Cl₂ to oxidize and precipitate As and Pb. After removal of the precipitate, the anolyte is treated with Ni powder to remove Cu. Following a filtration and addition of further chlorine, the pH is maintained at 4.0-5.0 by treatment with NiCO_3 . This causes oxidation and precipitation of Co. After removal of the latter, the purified electrolyte is transferred to the cathode compartment, in which enough hydrostatic head is maintained to prevent the entrance of anions from the anode compartment. The electrodeposition from the purified electrolyte is carried out at up to 20 a. per ft.², without excessive "treeing." This current density is considerably greater than is possible with an all-sulfate electrolyte. The Ni deposit is darker and of coarser grain than that obtained from the all-sulfate bath, but of superior purity.

1601. RYMERSHOLMS GAMLA INDUSTRIE AKTIEBOLAG
Electrolytic Production of Metals. British Patent 625,585, June 30, 1949; Chem. Abs., vol. 44, 1950, p. 1835i.

Very pure Co, Ni, or Fe is produced by electrolyzing a formic acid solution of the metal at a pH value of 5.8-6.0 and 30°-35° C. temperature. A pulsating direct current will prevent polarization.

1602. SAVELSBERG, WALTER. [Newest Developments and Present State of Electrolytic Recovery and Refinement of Nickel, With Special Reference to German Conditions.] Metall u. Erz, vol. 31, 1934, pp. 222-226; Chem. Abs., vol. 28, 1934, p. 4666⁵.

Reviews the Orford methods, the processes of the International Nickel Co., the Haglund methods, and electrolytic recovery from chloride solution.

1603. SHCHERBAKOV, I. G., LOSHKAREV, A. G., AND LOSHKAREV, M. A. [Experimental Electrolytic Refining of Copper-Nickel Anodes at the Ufalei Works.] Tsvetnye Metal (U. S. S. R.), No. 8, 1940, pp. 75-78; Chem. Abs., vol. 36, 1942, p. 5431⁵.

Experiments were conducted for several months at the Ufalei Ni works. The average analysis of the anodes was 85.65 percent of Ni, 0.59 percent of Co., 1.62 percent of Cu, and 1.71 percent of Fe. Cathodic Ni conforming to the specification requirements for Ni was obtained by using the following: 40 gm. Ni per l. of electrolyte, 15-20 gm. of H_3BO_3 per l.; 10 gm. of NaCl per l.; pH 5; and cathodic current density, 130 a. per m.² Average results obtained: Current efficiency, 94 percent; energy consumption, 2,094 kw.-hr. per ton of Ni; scrap, 22.8 percent; slime, 7.6 percent. The elimination of Cu, Fe, and Co from the electrolyte does not present difficulties (3 refs.).

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